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THE CAMBRIDGE SERIES OF PHYSICAL CHEMISTRY

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INFRA-RED ANALYSIS OF
MOLECULAR STRUCTURE

Cambridge University Press

Fetter Lane, London

New York

Bombay, Calcutta, Madras

Toronto

Macmillan

Tokyo

Maruzen-Kabushiki-Kaisha

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INFRA-RED ANALYSIS OF MOLECULAR STRUCTURE

by

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Preface

IT is noticeable that no book in English exists which deals with the application of infra-red spectroscopy to the analysis of molecular structure. This fact made itself evident to us a few years ago at the outset of work in this region of the spectrum, and it is for this reason that we offer our book—with all its failings—to others who may undertake investigations upon molecular physics, and who approach the subject from the point of view either of the mathematician or of the physical chemist.

The theme is that of the interchange of energy between matter—gaseous, liquid and solid—and infra-red radiation. With the properties of such an energy flux we are but little concerned, and this serves to explain the omission of much that is interesting in the verification of different radiation formulae, and in the ramifications of pyrometry. Actual laboratory procedure for the circumscribed purpose in view claims a chapter to itself, whilst a selection of the most important mathematical conceptions—again strictly limited to the immediate aim—forms an appendix.

Our obligations to workers and publishers are considerable, and in this connection we acknowledge gratefully the permission readily granted by Professor Dreisch, Professor Havelock, Professor V. Henri, Professor Schaefer, Sir Robert Robertson, Dr Braunbek, Dr Darrow, Dr Meyer, Mr T. E. Allibone, the Council of the Royal Society, Messrs Longmans Green and Co., Messrs Julius Springer, Messrs Vieweg and Son, *The Astrophysical Journal*, *The Physical Review*, *The Journal of the Optical Society of America*, for reproductions of their work, or from their papers and publications. If through inadvertence we have failed to include the names of any of those to whom we are indebted, we ask their forgiveness, and offer them our best thanks.

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To Mr C. P. Snow we are especially grateful for the help he has given us, both in reading the proof-sheets, and in drawing our attention to a number of obscurities in the text.

It is impossible to close this preface without an expression of regret at the death of Fräulein Gerda Laski, which has occurred on the eve of going to press. She has done much in recent years to further the knowledge of the infra-red spectrum.

F. I. G. RAWLINS
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Cambridge
December 1928

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Introduction

OF recent years there has been a realization of the importance of the spectral regions known as the "near" and "far" infra-red, for the study of such radiation has proved a powerful weapon for the analysis of molecular structure.

For purposes of classification the near infra-red may be considered as the region extending from the extreme of the visible red to the infra-red as far as the wave-length 23μ (i.e. 23×10^{-4} cms.); this region is readily accessible by means of suitable prisms. The far infra-red extends from 23μ to the neighbourhood of 300μ , which marks the boundary of the beginning of the shortest electromagnetic waves. Waves above 300μ are generated most conveniently by means other than temperature radiation.

After early investigations in the infra-red by Melloni, Ampère and Herschel, the purely optical properties of infra-red rays, such as reflection, refraction, dispersion, absorption, with the occurrence of polarization, interference and diffraction, were examined in detail. Yet the growth of the physics and chemistry of the infra-red, unlike the study of phenomena associated with the interaction of matter and radiation of shorter wave-length, has been severely restricted until the last few years.

In the first place experiment needs the devising of powerful and constant sources of radiation, and the construction and calibration of instruments of exceptional sensitivity. These difficulties of technique, while not insurmountable, are greatly in excess of those which are inherent in similar operations in the visible or ultra-violet. Again, the attention of chemists was early attracted to the visible and ultra-violet rays because of their actinic properties: very few photochemical actions are effected by infra-red radiation.

Nevertheless, the infra-red is in many respects as important as the visible, and may in the course of time prove a valuable supplement

to X-rays in providing a method for the investigation of molecular structure.

Since the infra-red radiation consists of electromagnetic oscillations of a frequency which is slow compared with the normal rate of motion of electrons in atomic orbits, emission and absorption will only occur for charged masses moving at speeds which are some hundred times slower than electron velocities. These masses consist in general of charged ions. Thus the utility of the infra-red radiation lies in the fact that it gives a method by which the presence of rotating or vibrating doublets can be detected.

Until recently the chemical evidence had been thought sufficiently complete to distinguish between three distinct types of interatomic linkages; the heteropolar linkage, as found in a salt such as potassium chloride, the homopolar or covalent linkage, examples of which are found in molecular hydrogen and the carbon-hydrogen union in saturated hydrocarbons, and the coordinate covalent linkage, observed in numerous complex compounds. On the other hand, the evidence from physical methods of attack on the problem of linkage between atoms gave a conclusion seemingly at variance with the chemical evidence. The physical methods consisted in the determination of the electric moments of substances from their refractive index, and their polarizability from the phenomena of electrostriction and the temperature effect shown by their dielectric constants; from them a finite electric moment was assigned to substances which, from chemical evidence, were believed to have homopolar linkages. More recent chemical examination, especially upon organic compounds, strongly suggests that the original hypothesis of a purely symmetrical character of the homopolar linkage must be reconsidered. Though the magnitudes of the electric or magnetic moments of reacting species may eventually prove to be a determining factor in chemical reactivity, it appears to be certain that transition between the homo- and the hetero-polar linkage need not be so abrupt as was once considered to be the case.

We may note that the existence of an electric moment does not

necessarily indicate the presence of ions, for atoms under stress or deformation in such a way that the mass and electric centres of gravity are not coincident provide such moments. Hence the examination of the infra-red spectra of substances identifies linkages which are not truly homopolar. In many cases it is possible to obtain values of the electric moments concerned, and these can be compared with the values which might be expected if true heteropolar linkages were present. The magnitude of the electric displacement can then be calculated.

Distinct advances have lately been made in the measurements of the absorption spectra both of certain solids and of gases. Identification of absorption spectra in crystals in the near infra-red with the presence of certain groups in the crystal, e.g. NH_4^+ or CO_3^{--} , has led to the assumption that the absorption is due to the vibrations of the ions or polarized atoms within the group; approximate analysis has already been made of the number and position of the fundamental absorption bands to be expected from simple radicles. The near infra-red spectra of such solids are complex, as series of overtones and combination tones of the fundamentals are observed, and as yet no completely adequate account of the number and intensity of these has been given.

As well as these intra-ionic vibrations, there are inter-ionic vibrations. The latter give rise to the residual rays or Reststrahlen. These residual rays are situated between 30μ and 200μ , and are important in that their frequency is a function of the atomic weight; they are closely associated with the specific heat function.

The values obtained in this manner may be compared with those calculated by a variety of methods which we shall have occasion to discuss. It may be observed that, just as vibrations within a complex group such as CO_3^{--} can be assigned to periodic motions of the individual atoms or ions within the framework of the radicle, so we may anticipate that a number of residual rays may be found for substances which crystallize in forms of low order of symmetry.

It must be mentioned that substances like sulphur on examination by infra-red analysis are shown to possess definite electric moments. It is clear that sulphur is in fact pseudo-homopolar and that some group within the crystal must possess a moment, the value of which can be determined. In this way a beginning can be made upon the problem of the conditions of stability and crystal symmetry of such substances, on the lines already developed for heteropolar materials.

The pure rotation spectrum of diatomic heteropolar gases lies in the far infra-red, and the more complicated rotation-vibration spectrum in the near infra-red. From the pure rotation spectrum it is possible to calculate the molecular rotational moment of inertia, an operation which can similarly be conducted from analysis of the fine structure of the absorption bands. It is at present no more than an interesting speculation whether the moment of inertia of a gas molecule is a constant for all stages of excitation in the infra-red and over a wide range of temperature; it indeed seems possible that the rotational moment may increase as the temperature is raised, on account of the wider separation of the rotating atoms (an analogy may be seen to a governor). The values of the moments of inertia determined from this method may be compared with those found from the dielectric constant or the chemical constant of the gas. The identification of the two isotopic hydrogen chlorides is an illustration of the potential accuracy of this method for the estimation of the moment of inertia.

It appears now almost certain that the older quantum theory does not provide a mechanism sufficiently complete for the interpretation of all the energy levels to be found in the vibrational spectrum of simple diatomic gases. Very recently the analytical principles of the de Broglie-Schrödinger wave mechanics have found increasing application in this field. Whilst it is as yet too early to state with confidence that this treatment is generally applicable, marked success has attended its use in such problems as the specific heat curves for hydrogen and the relative in-

tensities of the lines of the rotation-vibration spectrum of hydrogen chloride.

A refinement of theory may be needed to interpret the overtones, which analysis of the spectra of gases and solids shows not to be exact whole number multiples of the fundamental. This is an indication that the nuclear vibrations are not simple harmonic. It is possible that a more detailed examination of these displacements may give information on the form of the potential function for variable separation between the two nuclei.

Whilst the interpretation of the rotation and rotation-vibration spectra of diatomic gases has made satisfactory progress, the spectra of the more complex gases present formidable difficulties. Even in the case of the three gases carbon dioxide, water vapour and sulphur dioxide, the experimental data are not sufficient to express a final opinion on the shapes of these molecules and their moments of inertia. It is probable that the molecules of the two latter gases are definitely triangular in shape, and carbon dioxide molecules appear to be linear in the solid form and isosceles-triangular in the gaseous state. Ammonia seems to conform to the generally accepted pyramidal structure, but recently some doubt has been expressed as to the tetrahedral structure of methane.

Apart from a wealth of measurements of a low order of accuracy, little advance has been made in the analysis of the spectra of liquids in the near infra-red. While it has long been known that certain bands appear to be associated with definite atomic groups, no rigorous examination has been made of the fine structure of the spectrum of any substance in the three states solid—liquid—gas. A detailed analysis of the infra-red spectra of liquids and the study of magnetic rotation in the infra-red will both probably furnish important information on the nature of the liquid state of aggregation.

From what has been written it will be noticed that in infra-red spectroscopy we are dealing fundamentally with the problem of the nature of interatomic linkages; and it becomes possible to supplement, in solids at least, the information on interatomic binding

given by the X-rays. The study of materials with X-rays has now developed into a large and important subject, and one capable of providing solutions to numerous scientific and technical problems in the domains of physics, chemistry and crystallography. There seems little reason why the systematic use of infra-red spectroscopy should not also give valuable information in exactly similar fields of enquiry. It was this idea that led to the suggestion of a logical divorce of the infra-red from the other regions of the spectrum.

It has been said that the experimental technique is not an easy one. Specially designed optical apparatus, in which attention is paid to such factors as the refractive index of materials used for prisms, and the devices used for measurement of the energy density transmitted in various parts of the spectrum (a subject which leads to the discussion of the most suitable choice of thermopile-galvanometer or radiometer systems), are all of extraordinary importance in this particular field. Further, the infra-red absorption spectrum of—for example—a gas, does not consist of sharp lines, but of a series of bands, each possessing a definite shape and a finite width. For the evaluation of the head of the narrow band, as well as for the determination of the absolute intensity, it is necessary to take into account several factors, not only the resolving power of the instrument, but also the physical state of the absorbing material and the frequency of the radiation absorbed.

Whilst different aspects of the subject of infra-red spectroscopy are dealt with in detail in such well-known treatises as Baly's *Spectroscopy*, the National Research Council's Report upon *Molecular Spectra in Gases*, and Laski's contribution in *Die Ergebnisse der exacten Naturwissenschaften*, to all of whom our grateful thanks are due, the ever-increasing importance of the analysis of spectra in this region for the determination of molecular constraints, a subject of importance common to both physicists and chemists, and the existence of a number of interesting papers as yet not readily accessible to English readers, must serve as the *raison d'être* of this volume. Both Mr Rawlins and Dr Taylor have

spent a number of years in this laboratory in research in this interesting field, and in collecting, examining in a critical manner, and summarizing the widely scattered literature. The results of their labours are given in the following pages.

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Chapter 1: GASES

Introductory

THE chief incentive to the study of the infra-red spectra of gases is a desire to know more about the structure and properties of the molecule, a matter concerning physicists and chemists alike.

An investigation of the absorption spectrum of a gas in the infra-red shows that—generally speaking—a number of bands exist at intervals in the so-called near infra-red, say 1μ to 23μ , and yet another, apparently distinct, series makes its appearance in the far infra-red, down to some 200μ , or in fact as far as observation has yet gone in that direction by spectroscopic means.

The comparatively high frequency of the former group can be accounted for by supposing that it is connected with the vibratory motion of a diatomic (or polyatomic) molecule, since the forces holding together the atoms in a molecule are known to be large. This view of the origin of the near infra-red bands finds general acceptance; that is, it is assumed, for instance, in diatomic gases, that the two nuclei are performing oscillations along the line joining them, with a frequency of about 10^{14} oscillations per second.

Such a view would not however account for the series of bands at much larger wave-lengths: it was Bjerrum who suggested, in 1912, that these arose from rotations of the molecule as a whole. Nernst(1) had, some little time before, referred to the possibility of applying the quantum theory to molecular rotations.

Thus, the spectral range to be studied falls quite naturally into two regions, (i) that in the near infra-red, often referred to as the rotation-vibration spectrum, and (ii) that in the far infra-red in which lie the bands due to rotations alone—the pure rotation spectrum.

Experimentally the subject falls likewise into these two classes. In the near infra-red, 1 – 23μ , a prism spectrometer can be used,

because substances are available which are transparent in this region; in the far infra-red, in which the pure rotation spectra lie, dispersion can only be achieved with a grating.

Actually, gratings are frequently used for mapping rotation-vibration spectra, since the refinements of modern theory have brought the need of high dispersion into the foreground. Reference to the Appendix (p. 145) will show that these spectra might be expected from mathematical considerations to possess a complicated form, the fine-structure, which arises from simultaneous rotation and vibration of the molecule. This is illustrated by Fig. 1.

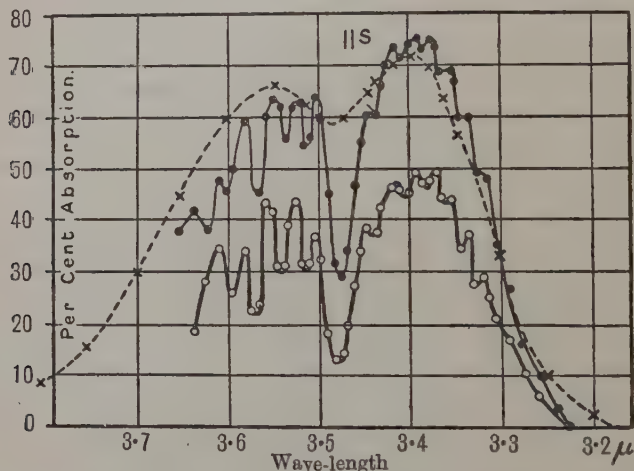


Fig. 1. Absorption of HCl.

The dotted curve shows the form of the absorption band in HCl as first obtained (by Burmeister) with comparatively low dispersion, while the lower curves are those due to Eva van Bahr(2) who, working with higher dispersion, succeeded in showing that the doublet found by Burmeister could be split up into twelve separate maxima.

More recent work by Randall and Imes(3), and Imes(4) alone, has shown a still greater number of subsidiary maxima and will be referred to in detail later on in this chapter.

Pure rotation and rotation-vibration spectra are connected by a useful relationship. Consideration of the motion in the two cases (see Appendix) shows that the frequency differences $\delta\nu$ between consecutive lines are the same. Since $\delta\nu = \frac{h}{4\pi^2 J}$, where h is Planck's constant ($= 6.55 \times 10^{-27}$) and J is the moment of inertia of the molecule about an axis through the centre of gravity and perpendicular to the axis of figure, this can only mean that the moment of inertia in the two states is almost the same. From a practical point of view this result is important, for it has enabled estimates of J to be obtained from observations in the shorter wave-length region, and, as has been explained, work here presents less experimental difficulties than elsewhere.

A knowledge of the molecular moment of inertia leads immediately to the inter-nuclear distance r , for if a diatomic molecule in the form of a dumb-bell rotates about the line perpendicular to the figure axis, then $J = Mr^2$, where M is given by

$$\frac{1}{M} = \frac{1}{m_1} + \frac{1}{m_2},$$

where m_1 and m_2 are the masses of the nuclei.

The expression for J becomes, in c.g.s. units,

$$J = \left(\frac{m_1 m_2}{m_1 + m_2} \right) 1.65 \times 10^{-24} r^2 \text{ gm. cms.}^2$$

if m_1 and m_2 are taken as the usual atomic weights, and

$$1.65 \times 10^{-24} \text{ gm.}$$

is the weight of an atom of hydrogen.

Thus, from the frequency differences $\delta\nu$ in the rotation-vibration spectrum or the pure rotation spectrum of a gas it is easy to obtain values for the moment of inertia J and the inter-nuclear distance r .

Since $\delta\nu = -\frac{c}{\lambda^2} \delta\lambda$ (where c is the velocity of light), it is clear that the optimum conditions are obtained when a band exists for investigation with the wave-length λ great, for then the spacing is wide, leading to more accurate results for J .

If the usual values for the constants h and c be taken, the spacing on a wave-length scale is given by

$$|d\lambda| = 5.5 \times 10^{-39} \frac{\lambda^2}{J}. \quad \dots\dots\dots(1)$$

To show that refined experimental arrangement is needed in order to take advantage of this equation, consider the case where $J = 10^{-39}$ gm. cms.² and $\lambda \doteq 3\mu$, both quantities being of the order of magnitude actually met with, then equation (1) shows that

$$|d\lambda| \text{ is about } 0.005\mu.$$

A band structure of this fineness probably represents the limit of experimental attainment.

In the presentation of results it is often convenient to express $\delta\nu$ or $\delta\lambda$ in wave-numbers. The wave-number being $\frac{1}{\lambda}$, the continual appearance in all the equations of the factor $c = 3 \times 10^{10}$ cms./sec. is avoided. Since most calibrations of instruments are carried out in λ rather than ν , the estimate given above indicates that a first necessity for work of this character is a spectrometer capable of giving trustworthy readings at such close settings. It may be noticed that this would need a density of 200 points per μ , in place of that of 20 or so with which much of the earlier work was done.

Moment of Inertia

Support for the original hypotheses upon which the theories of pure rotation and rotation-vibration bands are based is obtained mainly from the agreement between the values of J determined from them, and those which can be deduced from totally different considerations.

Two such methods may be mentioned:

(a) From the dielectric constant ϵ .

A considerable amount of attention has been given of late years

to the accurate determination of this constant. An empirical relation has been established between ϵ and the inter-nuclear distance r by Joachim and Wiśniewski(5).

Their equation is

$$\sqrt{\epsilon} - 1 = 22.02 \times 10^{19} r^3,$$

which they find is satisfied for diatomic molecules with the exception of hydrogen, for which

$$\sqrt{\epsilon} - 1 = 1 + 66.06 \times 10^{19} r^3.$$

If ϵ be known and r found, J follows.

(b) From the chemical constant i .

Eucken(6) has used this method of finding J for a number of gases. The value of i can be obtained from the vapour-pressure equation (which involves measurements of the specific heat as a function of the temperature), and is also given by the application of statistical mechanics in the equation for diatomic gases

$$i = \log \frac{(2\pi m)^{\frac{3}{2}} 8\pi^2 J \cdot k^{\frac{7}{2}}}{\sigma h^5}.$$

Here h is Planck's constant, m the molecular weight, k is Boltzmann's constant $= \frac{R}{N}$. The symmetry number σ is a factor depending upon statistical orientation, with which the present discussion is not concerned.

Thus J may be found from a value of i determined from thermal measurements. The limitations of this method, together with the literature on this subject up to the year 1925, have been discussed by Rawlins(7), and do not concern the present theme further. On the whole, fair agreement is found between values of J so deduced, and those obtained from band spectral data.

Hydrogen is an exception. Eucken(6) finds $J = 1 \times 10^{-41}$, whereas Dennison(8), using the wave-mechanics, obtains 4.64×10^{-41} from the specific heat curve, and Hori(9), from calculations upon the ultra-violet bands, 4.67×10^{-41} gm. cms.².

The "many-lines" spectrum yields the result $J = 1.8 \times 10^{-41}$. There seems little doubt that this molecular magnitude for hydrogen lies very close to the value 4.6×10^{-41} gm. cms.².

True Nature of Absorption Bands

From much that has already been said it will be clear that the infra-red absorption spectra of gases do not consist of sharp lines each of which is confined to a single frequency, but that they are composed of a series of bands each possessing a definite shape and a finite width.

It becomes therefore a matter of some importance to consider the factors upon which these characteristics of a band depend, chiefly for the reason that no accurate measure of the absolute intensity α is possible without taking them into account.

Dennison (10) mentions four factors:

- (a) The Doppler Effect.
- (b) An effect corresponding to the damping of a classical oscillator.
- (c) A resonance effect between neighbouring molecules.
- (d) An effect due to the limitation of the length of the wave-trains which may be absorbed by the molecules.

The physical state of the gas and the frequency to be absorbed will determine to a large extent which of these effects is the most important.

Dennison gives some simple calculations which show that it is only effect (d) that is likely to influence the shapes and widths of absorption bands in the infra-red, and therefore attention may be restricted to this alone.

The absorption coefficient P_ν over all frequencies is related to α , the total intensity of absorption, by the relationship

$$\alpha = \int_0^\infty P_\nu d\nu. \dots\dots\dots(2)$$

Also, the transmission T_ν for a spectrometer of infinitely high resolving power, and an absorption cell of length l , is given by

$$T_\nu = e^{-P_\nu l} \dots\dots\dots (3)$$

Owing to the low resolving power of the instruments generally employed, the region of irresolution has been very much greater than the true width of the line as given by equation (3). Thus, it appears that both the number of lines m of the grating used, and the width of the spectrometer slits, will influence the observed transmission curve. The accompanying sketch reproduced from Dennison's paper will make matters clear.

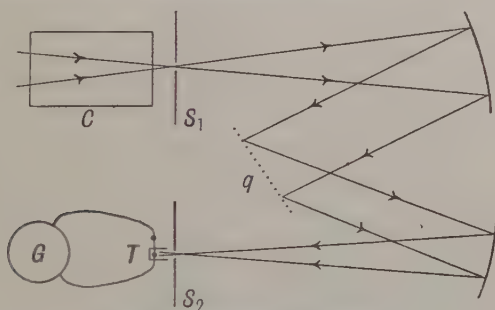


Fig. 2. Analysis of radiation.

The radiation, after passing through the absorption cell C of length l , is defined by a slit S_1 of width a . After diffraction at the grating q it passes through the exit slit S_2 of width b and reaches the thermopile T , which is in series with the galvanometer G .

The intensity with which the thermopile receives a frequency ν_i is ρ_{ν_i} , where ν_i is the calculated frequency falling upon the pile (i.e. the frequency corresponding to infinite resolution). The percentage transmission at ν_i is now

$$T_{\nu_i} = \frac{\int_0^\infty \rho_{\nu_i} e^{-P_\nu l} d\nu}{\int_0^\infty \rho_{\nu_i} d\nu}; \dots\dots\dots (4)$$

ρ_{ν_i} depends upon the resolution of the grating and upon the widths of the spectrometer slits.

If the intensity of the source is assumed to be independent of the frequency, there are two separate cases to consider:

(i) The slits are infinitely narrow.

Then
$$\rho_{\nu_i} = \frac{\sin^2 \{(\nu_i - \nu) \pi m n / \nu_i\}}{(\nu_i - \nu)^2}$$

for the spectrum of order n . (See (a) Fig. 3.)

(ii) If now $m = \infty$ (i.e. perfect resolution), and the slits S_1 and S_2 have the respective widths a and b , ρ_{ν_i} takes the form (b 1), whereas for the special case $a = b$, ρ_{ν_i} assumes the triangular shape (b 2).

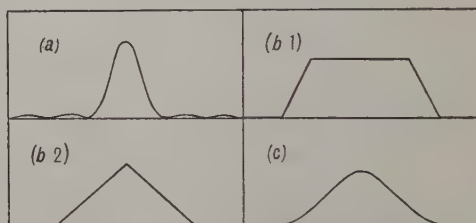


Fig. 3. Shapes of absorption bands.

Actually, however, since $m \neq \infty$, but $a = b$ in the usual practice, the form (c) is reached, which resembles very closely the Gauss error curve. In fact, no great error is committed in using this curve to represent ρ_{ν_i} .

Proceeding along such lines, Dennison arrives at two expressions of considerable importance for the area Abs. under the absorption line in its dependence upon the minimum value of the transmission T_{\min} , the true intensity α , the slit width a (both slits assumed to be of equal width), the cell length l , the number of lines on the grating m , the spectral order n and the molecular diameter* σ . (See however below.)

These formulae are

$$\text{Abs.} = (5.412 \alpha n \sigma^2 l)^{\frac{1}{2}} / (\pi h m)^{\frac{1}{2}}$$

and

$$\text{Abs.} / |\log_{10} T_{\min}| = 2.42 \alpha.$$

* N.B. σ in this connection must not be confused with the symmetry number of the previous section.

The usefulness of these equations has been limited, because, up to the present, most workers have measured the position on the wave-length scale of bands in the infra-red, without concerning themselves with accurate determination of the absolute intensity. The possibility of a direct calculation of intensity based upon the new wave-mechanics and also the feasibility of an estimate of σ —the molecular diameter—from the equations just given, point to the need for further researches in this direction. Meanwhile, from the experimental data obtained upon HCl by Paton⁽¹¹⁾, who examined the rotation-vibration spectrum of this gas at three different temperatures, the theory leads to a value for $\sigma = 10.6 \times 10^{-8}$ cms., whereas from viscosity measurements $\sigma = 5 \times 10^{-8}$ cms. That σ , as derived from these considerations of intensity, is some eight times larger than the distance between the nuclei in HCl is not surprising, for σ in Dennison's work really represents the least distance to which one molecule can approach another molecule without mutual alteration of phase (that is, interruption of the wave-trains).

That σ , however, comes out to be of the right order of magnitude is satisfactory support for the view that effect (d) is of great weight in its influence upon the form of absorption curves.

It is necessary to notice that the underlying principle of the theory already outlined is that of the kinetic theory of gases with its conception of interaction between elastic spheres, and that therefore strictly consistent results could only be expected when the mean free path is very great compared with σ . Actually, in Paton's work, the mean free path was less than ten times the molecular diameter, and an investigation at reduced pressure is clearly needed in order to test how accurately σ can be found by infra-red absorption methods.

Considerations based upon a knowledge of absolute intensity of infra-red bands may be used to obtain an estimate of the effective charge ϵ .

In this way, Dennison finds

$$\epsilon = (0.199) \times 4.77 \times 10^{-10} \text{ E.S.U.,}$$

which may be compared with Zahn's⁽¹²⁾ results; these yield a value

ϵ' derived from the electric moment

$$\epsilon' = (0.171) \times 4.77 \times 10^{-10} \text{ E.S.U.}$$

Again, experimental work on spectra due to Bourgin (13) leads to a value $(0.173) \times 4.77 \times 10^{-10}$.

It seems likely that of these Dennison's is the most accurate, for it takes into account the perturbations between the anharmonic vibration and the rotation. Zahn's figures are not strictly comparable with the others, for they refer essentially to a different property of the molecule.

The Spectra of Gases

In the following pages the most important researches of recent years dealing with the infra-red spectra of gases are considered. These include pure rotation spectra, rotation-vibration spectra, emission spectra, together with a brief mention of some observations upon the atomic (line) spectrum of hydrogen up to the limit of photographic recording and the solar work undertaken at the Mount Wilson Observatory.

[The reader who is not familiar with the mathematical treatment of the subject may find the definitions below helpful. Reference may also be made to the Mathematical Appendix to this book (p. 142).

For rotation of a molecule of moment of inertia J ,

$$\text{Energy of rotation } E_m = \frac{m^2 h^2}{8\pi^2 J},$$

and so the rotation spectrum is given by

$$\nu = \frac{m_1^2 h}{8\pi^2 J} - \frac{m_2^2 h}{8\pi^2 J},$$

where $m_1 - m_2 = \Delta m = \pm 1$; m has any integral value.

For vibration of the molecule,

$$\text{Energy of vibration } E_n = nh\nu_0(1 - nx),$$

where n is any integer.

For rotation and vibration together

$$E_{n,m} = nh\nu_0(1 - nx) + \frac{m^2 h^2}{8\pi^2 J},$$

and so the rotation-vibration spectrum will be given by

$$\nu = \frac{E_{n_1} - E_{n_2}}{h} + \frac{m_1^2 h - m_2^2 h}{8\pi^2 J}.$$

It will be seen that, for one change in vibrational energy, there can be several in rotational; and so is explained the fine structure of a rotation-vibration band. Any value of m may change to either $m+1$ or $m-1$. All lines in a band which are due to $m \rightarrow m+1$ are said to belong to the *P* branch; lines due to $m \rightarrow m-1$ to the *R* branch. This is represented by Fig. 4.

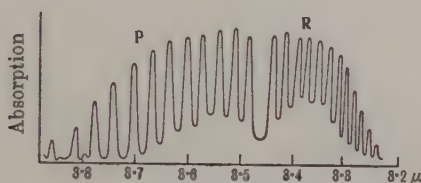


Fig. 4. Absorption of HCl at 3.46μ (Imes).

In certain cases the transition $\Delta m = 0$ is allowed (vibrational change only, no change in rotation); and from the above equation

$$\nu = \frac{E_{n_1} - E_{n_2}}{h}. \text{ Such lines are called a } Q \text{ branch.}$$

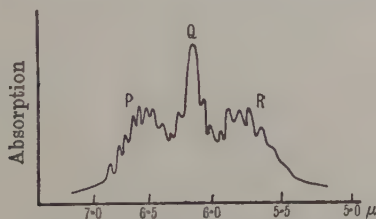


Fig. 5. Absorption of NH_3 at 6.132μ (Robertson and Fox).

It must be stressed that m itself need not be zero; it is Δm which is zero.]

Pure Rotation Spectrum of a Diatomic Molecule

In an important paper Czerny(14), using a modification of Rubens' original method, was able for the first time to observe the pure rotation spectrum of a diatomic molecule (HCl). He used a diffraction grating and found no less than seven bands between 42μ and 100μ , which show almost constant differences of wave-number.

A slight divergence from absolute constant difference can be represented by a small cubic term in the rotational quantum number; this term arises from the alteration of moment of inertia with angular velocity.

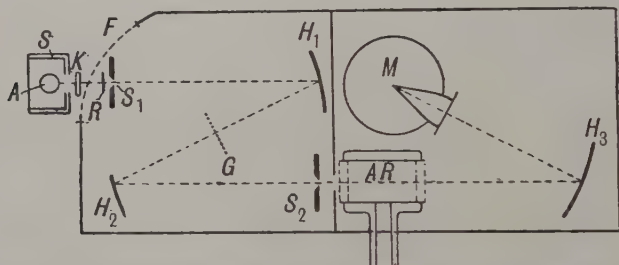


Fig. 6. Czerny's apparatus for absorption in the far infra-red.
A=source of radiation, *G*=grating, *AR*=absorption cell,
M=radiometer.

The following expression gives the frequencies

$$\nu = 20.794m - 0.00164m^3. \quad (m = 1, 2, 3, \dots)$$

The work is of striking theoretical importance. If one takes the rotational energy $E_m = \frac{h^2 m^2}{8\pi^2 J}$, the frequency is equal to $\frac{h}{8\pi^2 J} (2m + 1)$. On the other hand, the introduction of half quanta, that is, the writing of $(m - \frac{1}{2})$ for m , leads to

$$E_m = \frac{h^2}{8\pi^2 J} (m - \frac{1}{2})^2,$$

and

$$\nu = \frac{h}{8\pi^2 J} (2m).$$

From a comparison of the expressions of the frequencies

$$\nu = \frac{mh}{4\pi^2 J} + \frac{h}{8\pi^2 J} \quad (\text{whole quanta})$$

and

$$\nu = \frac{mh}{4\pi^2 J} \quad (\text{half quanta})$$

it is clear at once that the presence or absence of the constant term $\frac{h}{8\pi^2 J}$ will decide which is correct. Czerny found no constant term, thus producing convincing evidence for the existence of half quanta, in direct accord with Heisenberg's Quantum Mechanics.

In a recent communication Czerny⁽¹⁴⁾ describes an extension of his work to the other halogen halides, HF, HBr, HI. Taken together these two papers may be regarded as a classical contribution to the subject. It appears that the comparatively straightforward rotation spectrum of the HCl type is present for the other members of the family and a number of suggestive molecular constants are given. The following values are found for the fundamental ν_0 , and J_0 .

Gas	ν_0	J_0
HF	4003 cms. ⁻¹	1.345×10^{-40} gm. cms. ²
HCl	2939 „	2.656 „
HBr	2590 „	3.314 „
HI (see later)	2272 „	4.309 „

A somewhat remarkable relation is that between the B 's $\left(= \frac{h}{8\pi^2 J_0} \right)$, which stand very nearly in the ratio 10:5:4:3 to each other.

Czerny has also noticed that there is a fixed relation between the values of ν_0^2 and $2B$.

		$\nu_0^2/2B$	
Thus:	HF	3895	} nearly constant,
	HCl	4146	
	HBr	4018	

a fact to which Kratzer had devoted attention before. Looked at in the following way, this is significant. Suppose, as is true to a first approximation, that the vibrations are simple harmonic, then,

in the notation already used, $2\pi\nu_0 = \sqrt{\frac{K}{M}}$.

Then
$$2B = \frac{h}{4\pi^2 J_0} = \frac{h}{4\pi^2 M r_0^2},$$

from which $\frac{\nu_0^2}{2B} = \text{const. } K r_0^2$; that is to say, for these compounds the binding of the nuclei at equilibrium is inversely proportional to the square of the nuclear distance apart. This at once enables an estimate to be made of ν_0 for HI which works out at

$$(\nu_0)_{\text{HI}} = 2272 \text{ cms.}^{-1},$$

or $\lambda = 4.40\mu$. Now this rotation-vibration band had never been investigated, not even in the classical work of Imes. Czerny accordingly set up a fluorite-prism spectrometer in order to look for this band which (with the known value of J_0) should be a doublet with absorption maxima at 4.35μ and 4.56μ . Unfortunately, the shorter wave-length component falls near the CO_2 absorption at 4.27μ , which hinders accurate work, as a mere trace of CO_2 in the room will considerably increase the absorption.

However, Czerny observed one band at 4.53μ (no doubt the component at 4.56μ) and another at 4.30μ (presumably the 4.35μ component). The differences due, in the latter case, to the presence of CO_2 are striking. The author is satisfied that these results are real, though, as he points out, for HI the bands are very weak.

In a third paper, Czerny⁽¹⁴⁾ gives an interpretation of his results on the basis of the wave-mechanics. Although the theoretical conclusions remain the same, the values for J_0 come out smaller. Thus the new figures are

	J_0
HF	$1.322 \times 10^{-40} \text{ gm. cms.}^2$
HCl	2.617 "
HBr	3.267 "
HI	4.253 "

A slight difference is noticeable also for the fundamental frequency ν_0 .

In this work of Czerny's it is important to notice that a new refinement is introduced. ν refers to the rotational frequencies throughout, and is given, for all the halogen hydrides, by an expression of the type

$$\nu = am - bm^3, \quad (\text{half quanta are used})$$

where a and b are constants. ν_0 , on the other hand, is the fundamental vibration frequency found from the short infra-red spectrum (except for HI). The reason is this: J_0 is the molecular moment of inertia, assumed free from modification by centrifugal forces: another factor, a function of ν_0 , enters as soon as the above simplification for J_0 is removed. In other words, pure rotation spectra appear to be influenced by the vibrational term. Hence the value of Czerny's remark on the relationship between ν_0^2 and $2B$.

Pure Rotation Spectrum of a Triatomic Molecule H_2O

The pure rotation bands of water-vapour have had a history, and, together with the outstanding work of Czerny just described, form the whole of our experimental knowledge of far infra-red spectra in gases.

Paschen and Rubens found, for water-vapour, about 40 lines (with rather imperfect resolution) between 9μ and 100μ , and Eucken⁽¹⁵⁾ tried with varying success a number of empirical formulae to represent the frequencies. His expressions were (p integral)

$$\nu = \frac{p}{400}, \quad \text{or} \quad \nu = \frac{p + \frac{1}{2}}{424}.$$

A number of the more intense lines lying between 9μ and 20μ fitted either

$$\nu = \frac{p}{173}, \quad \text{or} \quad \nu = \frac{p + \frac{1}{2}}{180},$$

equally well: a final choice being impossible on account of the feeble resolution.

From an experimental point of view the work of Witt⁽¹⁶⁾ is of interest. He uses concave reflection gratings of spacing 1 mm. and 0.5 mm., which give a considerable increase in resolution. For the immediate purpose it is enough to mention that he has explored the region from 50μ to 180μ and finds a number of lines undiscovered by Rubens. The expression

$$\nu = a(n + \frac{1}{2}),$$

when $a = 16.85$ or 24.55 respectively for the two series, obviously pretends to be little more than a rough guide.

Further work on pure rotation spectra offers an attractive field of enquiry, for the advent of the new mechanics tends to focus attention sharply on this spectral region. Naturally, it is only polar molecules (e.g. HCl), possessing a permanent electric moment when at rest, which could be expected to produce pure rotation bands.

Rotation-Vibration Spectra

It is true to say that most of the work in the infra-red has been done in the region of higher frequency (λ between 1μ and 15μ). The reason for this is mainly experimental. A number of acute practical difficulties present themselves in the far infra-red region, as will become apparent in the chapter dealing with technique, while in that portion of the spectrum containing rotation-vibration bands, dispersion is possible by means of prisms (with sylvine even as far as 23μ) and the trouble of obtaining sufficient energy—although by no means absent—is yet fairly easily surmountable.

Because of this comparative ease of technique there is considerable data in this part of the subject; from it have been made notable advances in our knowledge of molecular physics.

(i) *Diatomic molecules: HF, HCl, HBr, HI, CO.*

The earlier work, the chief object of which was to deduce, according to classical mechanics, the molecular moment of inertia from the doublet separations, is referred to in the Appendix. For such a project, the hydrogen halides were convenient and were investigated by Burmeister(17). Eva van Bahr(2), working with HCl, was the first to obtain a fine structure. Brinsmade and Kemble(18), as well as extending the analysis of the HCl band at 3.4μ , were able to detect the existence of the first harmonics (also doublets) for HCl and HBr.

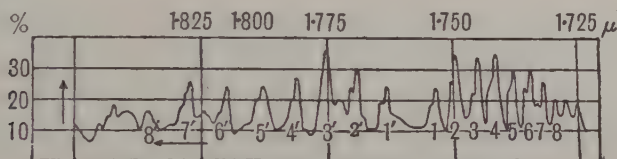


Fig. 7. Absorption of HCl at 1.76μ (Imes).

Probably the greatest refinement yet reached in this type of work was that accomplished by Imes(4) in 1919, using an apparatus consisting of what was practically two spectrometers in tandem, the first working on the Littrow principle with a rock-salt prism of large size, but with an angle of only 18° , the second with a reflection grating. In this way, overlapping of spectral orders was avoided, and the dispersion of the system was very great. Such an arrangement was essential if advantage was to be taken of the comparatively wide spacing of the lines given by HF, HCl, HBr.

It should be recalled that, to a first approximation, the moment of inertia is inversely as the frequency differences. The accuracy was such that it was feasible to obtain evidence of the existence of the isotopes of chlorine Cl^{35} and Cl^{37} .

Imes' graph for the first harmonic $2\nu_0$ (at 1.76μ) in HCl shows a number of subsidiary arrests which always make their appearance on the long wave-length side of the chief maxima. (See Fig. 7.)

Now ν_0 depends both upon the reciprocal binding forces between the nuclei, and also upon their masses. Thus, for a couple of isotopes, while the binding forces are the same, the masses are different, giving rise—for Cl^{35} and Cl^{37} say—to two rotation bands slightly displaced with respect to each other. The subsidiary maxima arise from Cl^{37} , which is only present to the extent of 1:3·5 of the amount of Cl^{35} (chief maxima).

If M is the reduced mass,

$$\text{then} \quad \frac{1}{M^{35}} = 1 + \frac{1}{35}$$

$$\text{and} \quad \frac{1}{M^{37}} = 1 + \frac{1}{37};$$

$$\text{and, since the frequency } 2\nu_0 = \sqrt{\frac{\text{force per unit displacement}}{M}},$$

$$\begin{aligned} \therefore \frac{\delta\nu}{\nu} &= \frac{1}{2} \delta \left(\frac{1}{M} \right) = \frac{1}{2} \left(\frac{1}{M^{35}} - \frac{1}{M^{37}} \right) \\ &= \frac{1}{2} \left(\frac{1}{35} - \frac{1}{37} \right) = \cdot 00077, \end{aligned}$$

$$\text{or, since} \quad \delta\lambda = -\frac{\delta\nu}{\nu} \lambda,$$

$$\begin{aligned} \delta\lambda &= -13\cdot54 \times 10^{-8} \\ &= -13\cdot54 \text{ \AA}. \end{aligned}$$

The negative sign shows that $\lambda_{\text{Cl}^{35}}$ is less than $\lambda_{\text{Cl}^{37}}$, in accordance with observation. Imes finds by experiment $|\delta\lambda| = 14 \pm 1 \text{ \AA}$. Such an indication of isotopes has been considered theoretically by Loomis(19) and by Kratzer(20).

Plyler(21) suggests that some curves obtained by him in the near infra-red show a similar effect in crystals, and he considers the subsidiary arrests observed furnish evidence of the presence of isotopes of the metal. It is hardly possible to credit this, since he is dealing essentially with the internal oscillations of a complex group, and not with any mode of vibration of the metal ion.

A number of other researches relating to the rotation-vibration spectrum of HCl can only be briefly indicated. Hicks and Mitchell(22),

using the results of the work of Colby, Meyer and Bronk⁽²³⁾ on the bands at 3.4μ and 1.7μ (those corresponding to vibration switches $0 \rightarrow 1$ and $0 \rightarrow 2$), have calculated the specific heat and entropy of rotation-oscillation. The latter quantity comes out at

43.17 with the Lewis constant;

or 43.40 with the Tetrode constant.

This example shows the way in which spectral data can contribute to the knowledge of thermodynamic constants.

A hope for the future may be expressed here. The new mechanics have led to some doubt upon the polar nature of the hydrogen halides (even HCl). An experimental determination of the rotational specific heat C_r as a function of the absolute temperature near 12° —if not too intractable a problem—would go far towards clearing up the nature of these compounds. Theory demands a maximum in this temperature region for the case of a true dipole.

The curve should rise about 10 % above $\frac{C_r}{R} = 1$, and then approach this value asymptotically.

Kemble and Bourgin⁽²⁴⁾ and Bourgin alone⁽²⁵⁾ have investigated intensity ratios for HCl. They find

$$\alpha = \frac{\bar{p}}{\nu^3} e^{-E''/kT}.$$

α is the area under the absorption coefficient curve on a frequency scale for the line in question. \bar{p} is the mean statistical weight of the two states involved in the transition, of which E'' is the lower energy value.

They used a quartz spectrometer, and took absorption curves for six different gas cells ranging in length from 0.1 cm. to 3 cms. By plotting a graph showing the area under the absorption curve against tube length they found α .

Again, in the second paper quoted, some evidence has been found for the isotope effect at the HCl fundamental (3.4μ).

A bismuth-silver vacuum thermopile was used. This research yielded two figures of interest for the Einstein probability coefficients,

$$B_{0,1} = 5.1 \times 10^{15} \text{ for the first line of the } R \text{ branch,}$$

$$A_{0,1} = 58 \text{ for the first line of the } P \text{ branch.}$$

Finally, Becker(26) has worked with a double prism spectrometer upon the HCl band at 3.4μ . While it must be remembered that all spectroscopic work must be done with slits of finite width, from this research an estimate may be made of the true half-breadth of the lines.

Beyond the hydrogen halides the only diatomic polar molecule submitted to infra-red spectral investigation is carbon monoxide. This has had quite an interesting history of its own. Burmeister(17) resolved the fundamental rotation-vibration band into a doublet, and deduced the moment of inertia on classical lines. Brinsmade and Kemble(18) detected the first overtone (a doublet), while Schaefer and Thomas(27) have found the second harmonic. Burmeister obtained, using a fluorite prism, $J = 14.6 \times 10^{-40}$, from the doublet at 4.6μ . (The separation was $120\mu\mu$.) Schaefer and Philipps(28) found J from the first harmonic ($\lambda = 2.35\mu$). They did ten measurements and had the advantage of working with the high dispersion of a quartz prism. The separation was $30.55\mu\mu$, leading to a value of $J = (14.8 \pm 0.3) \times 10^{-40}$, a satisfactory confirmation of Burmeister's work. Lowry (29) has used the Sleator-Imes apparatus in a search for the fine structure. None was found. It is hardly thinkable that such is really the case: this is one of the problems pressing for solution.

The CO doublet already discussed has its centre at 4.6643μ according to Lowry. Eucken(30) has collected the following values for the moment of inertia of CO, which may be compared with that just given:

$J \times 10^{40}$

14.7

no authority given.

15.8

from the visible spectrum.

14.7

from the vapour-pressure curve.

14.1

from Laski's molecular model.

Matossi(31) in an interesting short paper compares the deformability α of CO from the electric moment \mathbf{p} , and from the classical measurements of refractivity. α and \mathbf{p} are connected by the equation $\mathbf{p} = \alpha \mathbf{E}$, where \mathbf{E} is the electric intensity. This is evidently the analogue of Hooke's law (stress proportional to strain), and α may be considered as the electric moment per unit field.

The result of Matossi's analysis is

$$\alpha (\text{from } \mathbf{p}) = 1.10 \times 10^{-24} \text{ c.g.s.,}$$

$$\alpha (\text{from refractivity}) = 1.73 \times 10^{-24} \text{ c.g.s.}$$

Kliefoth(32) has performed, in Professor Schaefer's laboratory, a number of experiments upon electrostriction in gases—the change in volume upon application of an electric field. The details of this investigation are outside the scope of this book, but the point of immediate consequence is that the molecules O_2 and N_2 are shown definitely to have a zero moment. This explains the complete lack of rotation bands in these gases.

In concluding this section it may be remarked that so far no evidence of the existence of a Q branch has been brought forward for a diatomic molecule.

(ii) *Polyatomic molecules.*

A considerable amount of information about the form of triatomic gaseous molecules has been obtained as a result of work in the short infra-red.

The question at issue is generally: Is such a molecule linear or triangular in form? Interesting cases present themselves in carbon dioxide and water-vapour. X-rays have joined in the quest by proving quite definitely what structure these compounds possess in the solid form: it is of more than ordinary interest therefore to see to what results we are led from absorption spectra in the gaseous state.

CO_2 . Schaefer and Philipps(33) have investigated this gas within

the range of frequencies accessible with prisms of quartz, fluorite and rock-salt. Bands of high intensity are found at

$$2.72\mu, \quad 4.25\mu, \quad 14.87\mu,$$

and it is probable that these are due to fundamental modes of vibration. Now a triangular form, if isosceles, has three characteristic oscillations, and hence the supposition is that CO_2 is a very thin isosceles triangle of the form



Kliefoth finds a small electric moment ($\mathbf{p} = 0.2 \times 10^{-18}$) by the method of electrostriction, but the method is not one giving the highest precision.

Eucken⁽³⁴⁾ brings forward, from chemical and thermodynamical quarters, evidence which suggests that Schaefer and Philipps' results are compatible with a linear form*. It is concluded that there are three moments of inertia, two relatively large and one much smaller. Equality of the two large moments would result in a form to all intents and purposes linear.

Unfortunately, the chemical constant method of evaluating J only leads—for a triatomic complex—to a mean value $\sqrt[3]{J_1 J_2 J_3}$, when J_1, J_2, J_3 are the separate moments above mentioned.

This mean result is, according to Eucken, $J = 50 \times 10^{-40}$ gm. cms.². For the triangular model, calculation leads to a value of 150° for the angle at the carbon atom, and a distance of 1.02×10^{-8} cms. from carbon to oxygen.

* Recent work in Germany on the temperature variation of the dielectric constant of CO_2 leads, in Schaefer's opinion, quite definitely to the value zero for the electric moment, and thus provides strong evidence for the linear form. Schaefer, on this account, is prepared to abandon his predilection for the triangular model: but as yet the matter can hardly be taken as settled.

For a general discussion of the form of the CO_2 molecule, see Stuart, *Z. für P.* **47**. 457. 1928; and Barker, *Astro. Journ.* **55**. 391. 1922.

Dennison⁽³⁵⁾ using the new mechanics has attacked the problem of analysis of the possible motions. Since finality has not been reached, it is not desirable to go further into the matter here. It may be remarked, however, that difficulty is often found in accounting for the correct number of fundamentals, experiment yielding in some cases too few, and in one case at least (the solid CaF_2) too many.

The main theoretical predictions from Dennison's paper⁽³⁵⁾ are:

2.72μ band should be a pair of doublets,

4.25μ band should be a singlet and should have no Q branch.

Matossi⁽³¹⁾ has obtained a comparison of the values for the deformability α as he did for CO. He takes a triangular model of CO_2 and obtains

$$\alpha(\text{from } p) = 4.58 \times 10^{-25},$$

$$\alpha(\text{from refractivity}) = 1.43 \times 10^{-24}.$$

X-ray measurements lead to a linear structure for solid CO_2 , and the binding within the molecule is apparently ionic. The crystalline lattice is molecular, as would be expected from the latest work of Born, Bollnow, Pauling and Goldschmidt*. No information yet exists upon the spectra in the infra-red due to CO_2 in the liquid or solid state.

Wimmer⁽³⁶⁾ has studied the effects upon the band at 4.25μ produced by the introduction of other gases.

Stark and Blüh⁽³⁷⁾ claim that from their measurements of adsorption, CO_2 is linear in the gaseous state. This raises a profound question. Is a change from a triangular form to a linear one possible in the presence of a catalysing action of the adsorbing substance?

H_2O . This is mainly of interest on the experimental side—since no complete analysis has yet been achieved of the short infra-red bands.

Eva van Bahr⁽³⁸⁾, Hettner⁽³⁹⁾, Sleator⁽⁴⁰⁾, Phelps⁽⁴¹⁾—with a

* A brief review of this work is given by Rawlins, *Science Progress*. July, 1928.

special echelette grating and the Sleator-Imes apparatus—have all obtained the fine structure, the last named adding greatly to the number of known lines, and furnishing much improved detail, especially for the bands at 3.11μ and 6.26μ .

Progress with the H_2O spectrum will be slow; there appears to be a large number of lines present, the intensities and spacings of which seem to follow no definite law. In all probability the motion is little restricted: besides, the molecule may be devoid of axial symmetry*.

HCN. Barker(42) found no fine structure but observed a double band at 7μ .

SO_2 . Coblenz(43) early obtained a rough idea of the band spectrum of this gas. Its thorough investigation is an outstanding problem, more especially since much is now known of the CO_2 bands: some light on the difference in the properties of these two gases might be revealed. Kliefoth(32), by electrostriction, finds

$$p_{\text{SO}_2} = 1.7 \times 10^{-18}.$$

NH_3 . After early work by Coblenz, the first thorough investigation of this gas was undertaken by Schierkolk(44). A great range of frequencies was studied from 0.589μ (the sodium line) to beyond 14μ , and further resolution was obtained of the bands already known. Only mean values of the moments of inertia were forthcoming. They appear in various combinations. Schierkolk gives

$$\bar{J}(\text{at } 6.1\mu) = 2.72 \times 10^{-40},$$

$$J(\text{at } 10.5\mu) = 1.48 \times 10^{-40}.$$

On the basis of the presence of a Q branch and two spacing constants this molecule may be said to bear some likeness to methane, which is considered in the next section. NH_3 possesses axial symmetry, and it is quite possible that the rotation is not unlike that of CH_4 .

* Hund (*Z. für P.* 31. 81. 1925) considers that both the molecules of H_2O and H_2S are of triangular form.

Ammonia has again been subjected to analysis with high dispersion by Colby and Barker(45), who concentrated attention upon the band near 10μ . This seems to comprise two overlapping bands with zero or null branches at 10.3μ and at 10.7μ , and the general structure is alike for both. The convergence is small.

For the same normal vibration of the molecule, the authors suggest the following transitions:

$$\frac{1}{2} \rightarrow \frac{3}{2}, \frac{3}{2} \rightarrow \frac{5}{2};$$

or perhaps

$$\frac{1}{2} \rightarrow \frac{5}{2}, \frac{3}{2} \rightarrow \frac{7}{2}.$$

There is, as indicated before, a slight change in the line spacing, due to coupling; these spacings are 18.9 cms.^{-1} and 20.4 cms.^{-1} . There are invoked, to account for a number of bands previously known, two different types of transition:

- (a) one in which the second rotational number changes;
- (b) when this does not change.

The bands at 1.9μ and 2.2μ belong to (a). The bands at 6μ and its overtones, and that at 10μ , belong to (b).

Reasonable values for J are obtained, the NH_3 molecule being taken as a symmetrical pyramid.

The three gases NH_3 , PH_3 , AsH_3 have formed the subject of an extensive research by Robertson, Fox and Hiscocks(44). Their results for NH_3 agree in the main with those of Schierkolk, though the detail was carried to a greater degree of refinement.

If the view propounded by Hund(46) be accepted, that NH_3 is a tetrahedral molecule with N at the summit, it is impossible to bring the observed bands into line with his scheme of fundamentals and overtones. That the three gases possess very similar structures is shown by the remarkably constant ratios which persist between the positions of corresponding bands (see page 26).

It is clear that the spectra of these compounds are exceedingly complicated and it is as yet too early to say whether mathematical

analysis will succeed in unravelling the different modes to which the numerous bands—with marked *P*, *Q* and *R* branches—correspond.

The characteristic band in NH_3 at 15.908μ is possibly an overtone of the pure rotation band at about 63μ , and is associated with the small moment of inertia of about 0.3×10^{-40} gm. cms.².

Band	I	II	III	IV	V
NH_3 wave number	1630.9	3335.6	5083.9	6609.4	8250.8
PH_3 „	1125.0	2327.2	3413.7	4560.0	5608.5
AsH_3 „	1005.4	2121.9	3091.2	4161.5	5125.6
Ratio $\frac{\text{PH}_3}{\text{NH}_3}$	0.689	0.697	0.672	0.689	0.680
Ratio $\frac{\text{AsH}_3}{\text{PH}_3}$	0.893	0.911	0.905	0.912	0.914

CH₄. Cooley (47) analysed the fine structure of the rotation-vibration spectrum in great detail, and a number of features occur which are characteristic. The work was performed with a grating spectrometer. The bands at 3.3μ and 7.7μ show a large number of almost equidistant single lines, but at the centre of each band is a region of absorption, blotting out about three of the single lines. It is supposed that the centre of the band coincides with the edge of this absorption region on its high frequency side.

An experiment was performed with a greater quantity of methane in the absorption cell: it seems then that the maximum is displaced towards lower frequencies, and this is taken to indicate the presence of a mass of lines of which the intensities show a certain lack of symmetry, i.e. the intensity increases more rapidly on the short wave-length side than on the other.

These facts are taken as evidence of a zero branch. The spacing

is remarkable; that in the 3.3μ band being roughly twice that found for the 7.7μ band.

Dennison⁽⁴⁸⁾ has been able to give an explanation of this effect, which will now be considered in greater detail: it shows how valuable the results of refined infra-red spectroscopy can be in verifying theoretical possibilities in relation to molecular models.

To begin with, it is assumed that CH_4 is a regular tetrahedron with the carbon at the centroid and the hydrogens at the vertices. Certainly nobody has brought forward any convincing evidence of a preferred direction in methane; and at rest there should be no electric moment, a fact which is well established physically. Again, a tetrahedral form possesses three equal moments of inertia. Of the nine degrees of freedom, only four yield distinct frequencies, but the result is still further restricted, to a first approximation at any rate, since two frequencies would involve no change of electric moment. We are therefore left with only two fundamentals. Because a Q branch is found the electric moment does not always lie parallel to the invariable plane.

Theory shows that the spacing is only to be explained if the molecule has an electronic angular momentum of half a unit along a fixed axis. (Momenta are measured in units of $\hbar/2\pi$.) So far as rotation is concerned, the case is the same as for the simple rotator. Dennison then finds that if the electric moment \mathbf{p} does not lie in the axis of electronic angular momentum, nor perpendicular to it, the spacing becomes $\delta\nu = \hbar/8\pi^2 J$. On the other hand, if \mathbf{p} lies in such an axis, or perpendicular to it, then $\delta\nu = \hbar/4\pi^2 J$, i.e. double that just mentioned. Hence the characteristics of the bands at 7.7μ and 3.3μ respectively are accounted for.

Urey⁽⁴⁹⁾ some years ago investigated the specific-heat-temperature function of CH_4 , putting all three moments of inertia equal to 2.232×10^{-41} , and proceeded to obtain curves from expansion in series, as many workers have tried for hydrogen. The result can hardly be considered successful, especially at high temperatures where marked disagreements are noticeable between his curves

and those obtained from observation. Probably this is another instance in which the new mechanics will have to come to the rescue, for this seems to indicate some peculiarity in the constraints, which are perhaps neither wholly polar nor wholly non-polar. Dennison's(8) recent success with hydrogen gives cause for hope that this problem will not wait overlong for a complete solution.

A disturbing result, if it is confirmed, has arisen from some work of Ebert and Hartel(50). They have investigated the dipole moment of a number of substances of the form CX_4 , where X is either an atom or a radicle. They find a finite moment for CH_4 and even very small values for $C(CH_2Cl)_4$ and CCl_4 as well, and this may be thought to indicate that the structure may perhaps be pyramidal, though it cannot be tetrahedral*.

C_2H_2 , C_2H_4 , C_2H_6 . Levin and Meyer(51) have recently examined the absorption spectra of the gases acetylene, ethylene, and ethane, in the region between 2μ and 15μ , and have discovered the fine structure. They used the experimental arrangement previously designed by Imes and Sleator in their classical work on the halogen acids and water vapour.

For work between 2μ and 3μ , in place of the rock-salt filtering prism, one of asphaltum was substituted. Rock-salt windows were found to be satisfactory throughout for the absorption cells, which varied in length from 1 mm. to 20 cms. Dispersion was effected by means of gratings having the following characteristics.

<i>Between 2μ and 4μ.</i>	
2834 lines/cm.	Copper nickel surface
<i>Between 4μ and 8μ.</i>	
1134 lines/cm.	Aluminium surface
<i>Between 8μ and 15μ.</i>	
567 lines/cm.	Tin surface

* V. Guillemin Jr. has suggested a pyramidal structure for CH_4 ; see *Ann. der Phys.* 81. 173. 1926.

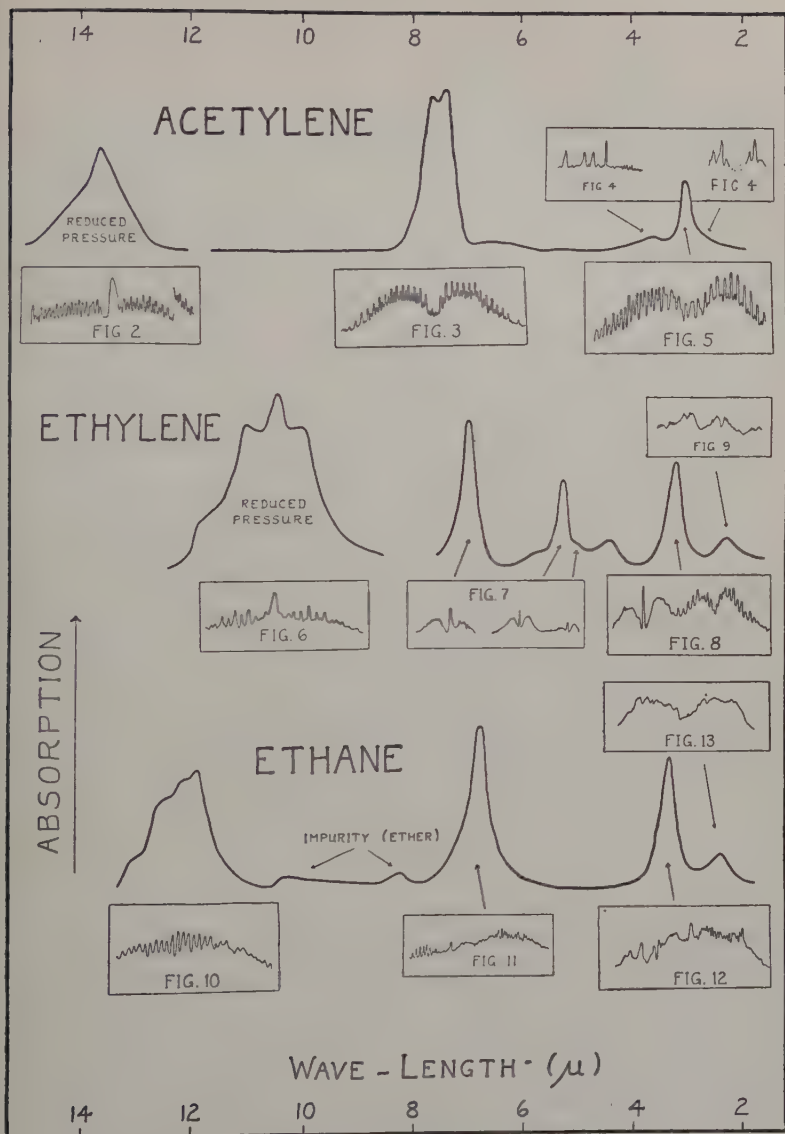


Fig. 8. (Levin and Meyer.)

C₂H₂. This gas possesses three marked regions of absorption, viz. at 13.7μ , 7.5μ , 3.0μ . In the first of these, *P*, *Q* and *R* branches were formed. The *P* and *R* show very clearly the feature of alternating intensities, but no convergence. The average spacing $\Delta\nu_2$ amounted to 2.35 cms.^{-1} . On the classical theory (see Mathematical Appendix) this leads to a value for the moment of inertia,

$$J_{\text{classical}} = 2.3 \times 10^{-39} \text{ gm. cms.}^2$$

or, according to the quantum expression,

$$J_{\text{quantum}} = 2.4 \times 10^{-39}.$$

The 7.5μ region shows a very faint *Q* branch—if any at all—the *P* and *R* showing alternating intensities as before. From this band

$$J_{\text{classical}} = 2.1 \times 10^{-39},$$

whereas from the separations near the centre

$$J_{\text{quantum}} = 2.4 \times 10^{-39}.$$

The 3.0μ band possesses *P* and *R* branches, the *Q* branch being absent,

$$J_{\text{classical}} = 2.0 \times 10^{-39}.$$

C₂H₄. The regions of absorption are approximately

$$10.5\mu, 6.9\mu, 5.3\mu, 3.3\mu.$$

The 10.5μ band showed a remarkably symmetrical form in the early work of Coblenz, and from this it is not difficult to anticipate the existence of a strong *Q* branch in the fine structure. This has been realized by Levin and Meyer, but it is not certain that the series of lines symmetrically arranged on either side, in the fine-structure analysis, are true *P* and *R* branches. The doublet separation, i.e. the distance from maximum to maximum of these probable *P* and *R* branches, amounts to 78.7 cms.^{-1} , considerably greater than in C₂H₂. The three remaining regions each show *P*, *Q* and *R* branches, the *Q* being intense.

C₂H₆. The very characteristic band of this gas at 12.2μ shows a single succession of maxima, increasing in intensity as the centre of the band is approached. This phenomenon has been observed before, in NH₃, and is taken to denote a series of *Q* branches.

The average spacing $\Delta\nu$ is 2.6 cms.^{-1} , with a slight convergence in the direction of lower wave-numbers.

The region around 3.4μ is not suitable for refined investigation, as its structure is found to be complicated by the superposition of the *Q* branch of methane.

It will probably by now have become clear that investigations upon infra-red spectra are beginning to pass out of the empirical stage to a condition of affairs more nearly approaching that achieved in research upon line spectra. If it be remembered how complex is the subject, both in theory and practice, it is hardly surprising that the state of knowledge of atomic or ionic complexes (molecules) is a fair way behind that in other regions of the spectrum less intractable.

An example will perhaps make this clearer.

In a long series of papers appearing in the *Comptes Rendus*, Deslandres has given a number of empirical rules by which frequencies may sometimes be represented. There is no doubt that his original band-spectrum expression gave valuable help in the early days, but these later suggestions are hardly of much assistance, for it is fast becoming within the realms of possibility to predict both the number of frequencies and (to a fair degree of accuracy) their relative intensities, either on the Heisenberg Matrix Mechanics, or perhaps more naturally from Schrödinger's theory.

The gain of having a definite dynamical basis is immense, and should act as an encouragement to workers in experimental physics to supply the theorists with data of the highest attainable precision. The means to this end will be taken up in the chapter dealing

with observational methods and technique. Meanwhile, the field of enquiry is large enough.

Infra-red Emission Spectra in Gases

For the sake of completeness, a very brief reference will be made to this subject. Most of the work was done by Paschen about 1896, and by Coblentz early in the present century. For instance, the former investigated the emission from helium in this region, and established marked bands at 1.1μ and 2.04μ . Coblentz mentions that H_2O shows no emission, whereas alcohol emits strongly between 2μ and 3μ . CO_2 has a characteristic emission at 4.75μ , a band which is also shown by $\text{C}_2\text{H}_5\text{OH}$, which however also has a continuous portion from 2μ to 4μ . No characteristic emission is known for ammonia. Purvis(52), in some more modern work, records a sharp maximum of emission for acetylene at 4.5μ , and for CO at 4.4μ .

It might appear that some practical value would attach to these emission lines for the purpose of calibration wave-lengths. The general problem of accurate calibration will be taken up in a later chapter, but meanwhile it may be convenient to say here that these emission bands, when plotted, have a decidedly rounded top, much too flat or extended to give the accuracy now aimed at in making a wave-length scale. The authors have found it safer to take as standards the absorption positions of a crystal such as calcite.

Molecular Models and Series Relationships

The main lines of evidence which the different types of infra-red spectra—pure rotation, rotation-vibration and emission—can contribute to our knowledge of molecular physics have now been reviewed, and a number of outstanding problems have suggested themselves as possible themes for future attack. It remains to make use of the observed results in an attempt to see, in a perfectly

general way, how far they have led to a satisfactory picture of the behaviour of molecular systems.

One thing is abundantly clear at the outset—the magnitude of the period of the electromagnetic fields in the infra-red will tell us nothing about molecular statics directly. For this line of advance, X-rays are responsible. It is then from dynamical considerations that the information must come. Force functions may be derived to fit the intensities and absorption frequencies experimentally observed. This procedure, which is strictly in accordance with the spirit of the wave mechanics, determines the nature of the forces which hold the molecule together.

For example: if it is desired to know the inter-nuclear distance r_0 at equilibrium of a diatomic gas molecule, the arguments are purely dynamical. It is assumed on the simplest view that a rotator in the form of a rigid dumb-bell performs the most restricted type of motion possible, and from the quantum relations between the frequency and the energy of rotation the moment of inertia J is deduced, and from that the required length r_0 .

The underlying steps here are seen to be in sharp contrast to the corresponding problem in a crystal, where the lattice constant is determined statically with the help of X-rays. It will become clear in the chapter on solids that it is only by circuitous routes, and by employing thermodynamic magnitudes, that “molecular” lengths can be found. Thus, the chief conquests of the infra-red worker will probably be in the dynamical behaviour of crystals as well as of liquids and gases. It may not be out of place to remind the reader that this, so far as spectra are concerned, forms part of a perfectly natural and logical system.

Thus, structural changes within the nucleus give rise to γ rays (λ about 10^{-9} cms.), orbital transitions of electrons to X-rays and optical spectra (λ 10^{-8} to 10^{-5} cms. approximately), and when the coupling of atoms or ions into molecules is considered, then transitions between different rotational or vibrational states produce infra-red bands (λ 10^{-4} to 10^{-2} cms.).

To these may be added the electronic transitions within the molecules, which give rise to the familiar band spectra, first classified by Deslandres. Partly for the sake of simplicity, and partly because results are not yet sufficiently consolidated, little mention has been made of the importance of these changes and their effects. In so far as they give rise to bands, the question need not concern us, for these fall at wave-lengths well outside the infra-red region, but in connection with electronic angular momentum and the existence of zero or null branches they have made their influence felt in the work already described. (See the treatment of gyroscopic motion for diatomic molecules by Kramers and Pauli⁽⁵³⁾.)

Another problem is connected with the relationship between electronic frequency and nuclear separation. This latter magnitude will naturally be changing in rotation-vibration spectra, and assuming that it is justifiable to use classical mechanics when dealing with motions in one of the Bohr stationary states, then Kemble and Van Vleck⁽⁵⁴⁾ have shown that in general the electronic frequency increases with decreasing nuclear distance. It is important to notice that this result is indecisive in that it refers to electronic frequencies as a whole. In experiments in which individual frequencies can be isolated it may fail to be verified by the facts. Kemble states that the moment of inertia may either increase or decrease when a molecule passes from a lower to a higher electronic state. Theory and experiment disagree as to the relative probability of the two events.

A study of the series relationships between the frequencies exhibited in the infra-red by a family of chemical compounds has often proved of considerable interest, and a typical example is the investigation of the set of hydrogen halides, HF, HCl, HBr, HI. The inter-nuclear distance and moment of inertia increase from member to member in the order of molecular weight, and the progressive shift of the vibrational frequency ν_0 towards higher values shows the alteration in closeness of the binding between the atoms.

The organic gases might appear to present a fertile field for an enquiry of this kind. Coblentz, as already mentioned, produced a mass of data many years ago, but the meagre density of his readings (sometimes not so much as ten points per μ) makes his work mainly of qualitative value for present-day purposes. The moments of inertia of these molecules are great, and consequently the fine structure of the infra-red bands will need a high degree of resolution for its observation. Even if this is achieved the theoretical difficulties of interpretation are very great; the problem of alternating intensities, which may be connected with the particular choice of quantum weights, is not yet fully solved. The use of such experimental work in its bearing upon molecular physics therefore seems doubtful.

The Dielectric Constant ϵ , and the Dipole Moment \mathbf{p}

The problem with which the last section concluded is closely bound up with the question of the inter-relationship between the dielectric constant ϵ of a gas, and its dipole moment \mathbf{p} .

Incidentally, Maxwell's expression $\epsilon = (\text{refractive index})^2$ for long waves will be remembered.

An analysis of this question on the basis of statistical mechanics led Debye(55) to the equation

$$\frac{3}{4\pi} \cdot \frac{\epsilon - 1}{\epsilon + 2} = \frac{N\mathbf{p}^2}{3kT} + N\beta.$$

N is Avogadro's number, k the Boltzmann constant, T the absolute temperature.

The distortion of the orbits of the electrons by the field brings in a small term β as an addition to the induced electric moment.

More recent work on this equation has been carried through by Pauli(56) and by Van Vleck(57). The former found that a coefficient 1.5367 should occur instead of $\frac{1}{2}$ in the first term on the right. It is significant however that Van Vleck, who goes into great detail based on the new mechanics, returns to Debye's factor $\frac{1}{2}$.

Another modification is due to Pauling(58). He asserts that the coefficient of $\frac{N\mathbf{p}^2}{kT}$ is not a constant at all, but a function of JT (J is the moment of inertia).

However, a difficulty arises which luckily is quickly disposed of by the matrix mechanics. Pauling uses even integers for the number of different orientations which may be assumed by the molecules in an electric field (the so-called statistical *a priori* probabilities) for the reason that the odd integers give rise to negative electric polarization, which is impossible. Kemble and Bourgin(24) in their work on the rotation-vibration intensities of HCl nevertheless find that 1, 3, 5, 7, ... is correct, in accordance with the summation rules of Fowler(59) and Dieke(60). Mensing(61) and Schrödinger(62) find that the angular momentum is zero for the state of lowest rotational energy, but the rotational energy itself does not vanish; this invalidates Pauling's conclusion. Barker(63) looked for the Stark effect in HCl with a negative result, which fits in with the work just quoted, and also provides additional support for the new mechanics.

Other Infra-red Investigations

There has been much work done in the short infra-red, not far removed from 1μ or 2μ , which, though not directly concerned with molecular physics, must be mentioned here.

In contradistinction to what has been the main theme so far, the first matter to claim attention is the mapping of the atomic line spectrum of hydrogen by Brackett(64) out as far as 4.5μ .

He set up a long discharge tube (like that used by R. W. Wood in his work on the Balmer series), and used the radiation from the central portion. A spectrometer with rock-salt prism, with a sensitive vacuum thermo-junction as receiver, was employed, with the result that five lines of the Paschen series—three of them new—were observed at frequencies given by

$$\nu = N \left(\frac{1}{3^2} - \frac{1}{m^2} \right), \quad m = 4, 5, 6, 7, 8$$

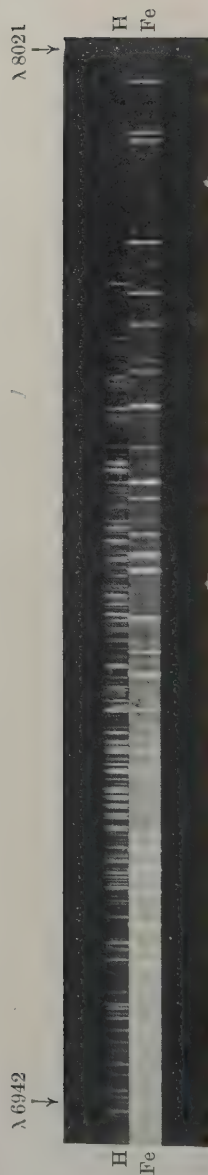


Fig. 9. "Many-lines" or secondary spectrum of hydrogen with are spectrum of iron for comparison (Allibone).

(N is the Rydberg constant), in agreement with the well-known Balmer formula.

Brackett was able to go a stage further than this, and succeeded in finding the first two members of the series

$$\nu = N \left(\frac{1}{4^2} - \frac{1}{m^2} \right), \quad m = 5, 6$$

which lie at the wave-lengths 4.05μ and 2.63μ . If the usual Bohr scheme is assumed for the energy levels, these correspond to falls of electrons from outer orbits to the third and fourth orbit respectively. For the long discharge tube already mentioned, it was observed that the first line of the series $\nu = N \left(\frac{1}{3^2} - \frac{1}{m^2} \right)$ increased in intensity more rapidly than the well-known line H_α (in the visible red) when the current was increased about fourfold through a section 7 mm. diameter.

Poetker (65) has also performed some extensive experiments on the spectrum of hydrogen, from 0.75μ to 1.07μ , using a photographic method which employed neocyanin plates hypersensitized by an ammonia bath.

Next comes some work undertaken by Allibone (66) on the so-called "many-lines" spectrum of hydrogen. It will be remembered that this peculiar spectrum is really the band spectrum of the hydrogen molecule. The reason for its unusual characteristics is that the moment of inertia is so small as to mask the ordinary appearance. Specially sensitized plates were used, and an idea of this spectral region can be obtained from the plate reproduced. Apparently, in order to reduce these lines to a formula a cubic term in m , Dm^3 , is needed.

No selective effect could be detected when a transverse magnetic field was applied. There was, however, a gradual broadening of all the lines.

The experimental equipment comprised a spectrometer provided with a diffraction grating having 14,500 lines to the inch, and quartz lenses. The dispersion was 25 \AA. per mm. and the tube was

used in the ordinary way, end on. A complete list of previous researches on this subject of the many-lines spectrum of H_2 is given in Allibone's paper. Three papers dealing with hydrogen come from Sandeman⁽⁶⁷⁾ and Allen and Sandeman⁽⁶⁸⁾, who have gone into the question of the bands in the secondary spectrum of this gas.

They find the bands spaced out at intervals of approximately 92 wave-numbers, and the suggestion is made that this system is connected with the existence of the molecule H_3 .

There remains some work on the solar spectrum in the infra-red to be included. Brackett⁽⁶⁹⁾ has mapped these lines from 0.89μ to 0.99μ , using dicyanin plates and the 15 feet concave grating at the Mount Wilson Observatory. Evidence is brought forward that there is a band due to water vapour between 0.93μ and 0.965μ . Of the solar lines proper 14 are due to iron and one or two to nickel.

A recent contribution to solar physics comes from Babcock⁽⁷⁰⁾, who has explored the "borderland" region, 0.687μ to 0.898μ .

Explosions

A subject of interest to the chemist and the chemical engineer is the part played by absorption and emission of infra-red radiation in explosive reactions.

Progress has been made in recent years by Callendar⁽⁷¹⁾, David⁽⁷²⁾ and others. The whole question appears to be complex (see the diagram given by Garner⁽⁷³⁾) but the following points may be considered.

In explosions of coal gas and air, as much as 25% of the energy of the flame and explosion is liberated in the form of infra-red radiation, the partition of which among the scale of wave-lengths is a function of temperature. Absorption of infra-red radiation in front of the flame is not a dominant factor. In a mixture of hydrogen and oxygen, for example, emission (flame) bands are found to which

no absorption bands are known to correspond. It may however be otherwise in some cases. When CO and O₂ are exploded, some 30–50 % of the total radiation from the explosion lies in the 4.4–4.5 μ band. Now Coblenz(43) found that a thickness of 5.7 cm. of CO at atmospheric pressure absorbs about 40 % of incident radiation for this band, from which it may be inferred that some pre-heating is present in advance of the CO flame. This might be considered as almost auto-catalytic in effect. David has produced evidence of pre-activation by infra-red radiation from a study of CO-air and CH₄-air reactions. According to his researches, the speeds of explosion are accelerated if immediately before explosion the gaseous mixtures are insulated by infra-red radiation corresponding to the absorption band of the gas. This acceleration takes place towards the end of the explosion, when a compressional wave has set in in advance of the flame. A “duration of life” of several seconds is suggested for molecules of CO and CH₄ under these conditions, which is in agreement with the energy distribution in flame and explosion spectra.

A number of recent observations by Garner, Johnson and Saunders(74) upon catalytic effects in CO and O₂ explosions (moist and dry) and infra-red emission spectra may be mentioned. Water and other positive catalysts greatly reduce the emission at 4.4 μ and 2 μ to 8 μ ; whilst up to the present no contrary effect of increase of infra-red emission has been observed. The authors however remark that “the possibility must not be overlooked that catalysis in the flame and explosion is always of this type.”

CONCLUSION

Although several examples have tended to bring out points of distinction between what must now be called “classical quantum theory” and the new mechanics, yet a number of remarks have been made as if only the older views, especially some of the more naïve conceptions of the planetary atom, held sway completely. The reason for this is that such were indeed the interpretations to

which various investigators were led as the outcome of their labours, and the time has not arrived when we can entirely discard a material view of the electron.

This expedient is forced upon us, for the achievements of de Broglie and Schrödinger have only as yet succeeded in considering the electron as a seat of pulsations, whilst the nucleus, with which infra-red spectra are to some extent concerned, is only taken as a source of potential, instead of being, in some way still unknown, also connected with the propagation of waves.

It is this which compels the retention of the cruder conception of the electron as a mass-point.

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Chapter 2: LIQUIDS

Introductory

THE explanation of infra-red spectra of liquids has nothing like the completeness of that which has been achieved for gases, or even solids. This suggests that the investigation of liquids is an attractive field of research, but it is only fair to say at once that the problem is a complicated one. The reasons are largely those which have made the knowledge of the specific heats of liquids so empirical and unsatisfactory.

Thus, in gases, as has already been pointed out, the reciprocal effects between molecule and molecule, except at collision, can safely be neglected, more especially if the order of time usually involved be taken into account.

In solids, it is possible to make some progress by imagining the constraints to give rise to vibrations of the charged centres of the crystal lattice about a position of equilibrium. That this is at best only a rough treatment and quite useless for many cases will become clear in Chapter 3. So far as mechanics are concerned, it is the simple characteristics of gases and solids which have been responsible for such rapid advance.

In liquids, we have the intermediate conditions, in that considerable binding between the molecules is present; yet the constraints are not sufficiently powerful to keep the vibration within limits that could possibly be considered "small." Hence it is clear that a far more difficult task is involved in laying a sound theoretical basis for the liquid state than is the case for the other phases. The potential energy is not a quadratic function of the co-ordinates, nor is it linear as regards temperature.

The fact of association tends to complicate the whole subject as to what group or groups are concerned in a vibration. Yet the transition between vapour and liquid is continuous at the critical

temperature, and since quantum behaviour is certainly present in gases, it may well be expected in liquids.

It is considerations such as these which have hindered the building up of a complete theory of the specific heat for liquids, much in the same way that they have affected adversely the attainment of a satisfactory "liquid dynamics."

Eucken(1) has made the attempt to apply Debye's theory as it stands for solids to monatomic liquids such as mercury (if monatomic they can be said to be). The justification for such a proceeding is that some liquids obey the law of Dulong-Petit fairly accurately. Still, neither this nor the work of Honda(2) can be said to carry any conviction in this particular.

Schultze(3) has examined the behaviour of the quantity $C_p - C_v$ for liquids very carefully (C_p is specific heat at constant pressure, C_v at constant volume). He finds the ratio $\frac{C_p}{C_v}$ very different from unity, whereas $C_p - C_v$ for organic non-associated liquids is usually between 10 and 11. It is generally smaller for associated liquids.

While it is unlikely that work on the infra-red spectra of liquids will yield results of deep theoretical interest, there are nevertheless a number of problems in which useful data can be obtained.

Perhaps chief of these is the series relationships in a set of homologous organic compounds. Here it has sometimes proved possible to ascribe some strong and persistent band to a particular linkage, e.g. the carbon-hydrogen band, when it is observed to occur throughout such a series. This subject is one that may be of interest to chemists in particular: it is to be regretted that the technique is so difficult that it appears to be impracticable to apply such observations as tests for purity and so on, in the same way as refractometry and polarimetry are used, even in industrial laboratories.

In this chapter, however, a number of examples will be noticed where a study of infra-red absorption bands has proved of value from a chemical point of view.

A drawback, which makes accuracy in wave-length determination quite low, is that the bands are usually very broad compared with those usually found in gases and solids. This imposes a minimum of strain on the finer performance of the apparatus.

The theory of strong electrolytes attempted some years ago by Milner, but now associated chiefly with the names of Debye and Hückel(4), is relevant to this discussion, in so far that it is its object to deal with the property of conductivity in solutions, and this in its turn hinges upon the nature of the ionic charges and the influence of the solvent. Fajans(5) considers that in a number of cases contact occurs between the dissolved particles, i.e. that there is no solvent molecule in between. Some interesting possibilities arising out of this will appear when we come to consider the infra-red spectra of solutions. It is well to bear in mind that although Debye and Hückel's contribution is usually referred to as the theory of "strong electrolytes," yet the concentrations to which their analysis is applicable are very low ($\frac{1}{100}N$). Also, the best work on infra-red spectra of solutions (say that of Reinkober) is scarcely sensitive enough to give trustworthy information about the displacement of characteristic frequencies with alteration in concentration.

A theme awaiting development is that of comparison of infra-red absorption wave-lengths between the liquid and solid—or gaseous—states for the same substance. Experimental difficulties are probably the cause of trouble here, but a certain amount of work has been done on a number of compounds, among which benzene may be mentioned. This work needs great refinement of apparatus, for experience shows that the shifts to be expected are quite small: small enough even to be overlooked except with very careful investigation. Yet the alteration in magnitude of the constraints in the two states would lead one to suppose that such a difference should exist.

Little is known of the influence of temperature on the position of the bands, or on their breadth. This subject, it will be recalled, has been attacked for gases (HCl), and it has found a place in work

on solids. Naturally, it is not to be expected that it would yield anything definite when applied to solutions, as the concentration itself is usually so greatly influenced by temperature, but in pure liquids some additional knowledge is feasible and would be welcome.

There is a great prevalence of absorption bands in liquids in the visible spectrum, a number of which are probably connected in some way with those of the infra-red. It is hardly likely that Haber's rule will apply, since this really amounts to the assumption of simple harmonic motion.

Victor Henri⁽⁶⁾ expresses the opinion that the infra-red and ultra-violet frequencies of a liquid are connected by integral relationships, and that this simple character is maintained when a number of bands are present in either region. This amounts in effect to a general acceptance of Haber's square-root rule, or some similar formula.

Up to the present, recent work on the structure and dynamics of the molecule* has not presumed to offer any explanation of overtones or harmonics of any but the very simplest of cases, and even then the subject is complicated. If anything is certain it is that exact integral relations are not to be expected; this is because of the anharmonic nature of the forces involved. Again, it is hardly justifiable to compare the characteristic frequencies observed (as Henri does) with the formula of Lindemann, for this is admittedly only valid at the melting temperature, and much doubt must arise as to what exactly is meant by the atomic weight (of a liquid) which enters into this expression. A difficulty arises too in fixing the value empirically of the numerical constant. The rotational motion postulated by Henri to account for some of his observed infra-red bands has, in the hands of Honda, failed to afford any satisfactory data upon specific heats.

From what has already been said it will have become clear that

* In the liquid state, as for gases and solids, it is generally agreed that the molecule is responsible for the effects observed in the infra-red, whereas the electron is concerned in the ultra-violet.

a treatment on the lines of that given in the chapter on Gases is possible. The following scheme recommends itself.

Examination of:

- (1) Pure liquids, and liquids and their vapours.
- (2) Solutions (liquid solvents).
- (3) Solid solutions and glasses.
- (4) Water of crystallization.
- (5) Liquid crystals.
- (6) Magnetic rotation in the infra-red.

(1) is most likely to be of value in tracing series relationships and offering possible verification of other chemical evidence;

(2) and (3) yield a considerable amount of data of physical-chemical interest;

(4) might equally well be in the chapter on Solids, but it brings out nothing of outstanding interest for that subject, whereas it finds a natural place in the present scheme;

(5) would repay much more attention than it has yet received;

(6) is mainly physical in nature, though it has not been fairly established on a theoretical basis.

(1) *Pure Liquids*

Coblentz has been responsible for the accumulation of a mass of data dealing with the absorption spectra of pure liquids, mostly organic substances. Since his work was done more than twenty years ago, and is accessible to those wishing to consult it (*Report of the Carnegie Institute of Washington*, 1905 onwards), the only reference that will be made to it here is the statement that many examples of series relationships were suggested. It must be borne in mind that, as mentioned in the chapter on Gases, it was Coblentz's custom to observe something like ten points per μ , and it is hence impossible to ascribe more than qualitative accuracy to his curves. This does not question the accuracy of his calibrations; it is merely wished to emphasize that, in order to fix the position of

a maximum of absorption, a great number of points near this maximum must be taken. This is necessary because both theory and practice agree that bands are by no means always symmetrical. It cannot be safe to draw the curve symmetrically between sparsely distributed readings.

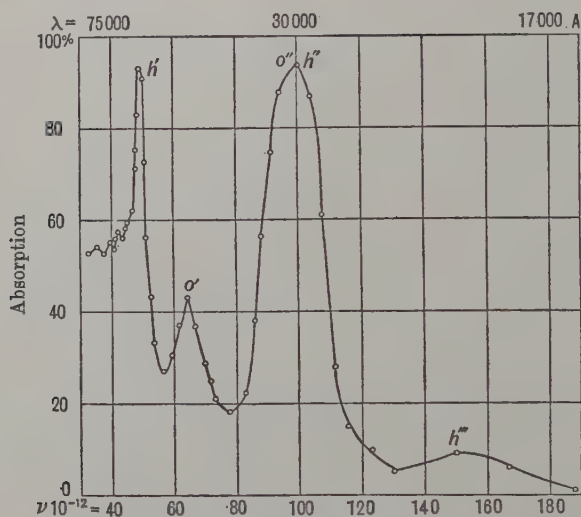


Fig. 10. Absorption of water in the near infra-red (Henri).

Water

Victor Henri(6) (*loc. cit.* page 159) gives curves for the short infra-red absorption of H_2O , both liquid and vapour.

The former shows an overwhelming number of bands, but the latter has only four distinct positions of absorption at 2.0μ , 3.0μ , 4.7μ , 6.26μ . It is difficult to give weight to these particular figures, for—as usual—the bands are very broad and apparently an average density of observed points of about 5 per μ was considered sufficient.

Collins(7), using two spectrometers to obtain high dispersion, has worked between 0° and 95° C. in order to find out the nature of the shift with temperature. He establishes a displacement

towards shorter wave-length with increasing temperature, and a marked increase of the intensity of absorption for the bands at 0.77μ , 0.98μ , 1.21μ . This latter effect is described as due to the presence of varying amounts of the polymers $(\text{H}_2\text{O})_2$ and $(\text{H}_2\text{O})_3$ at different temperatures.

In a recent contribution, Tamman(8) reports the outcome of some extensive researches on the "water" band at 4.7μ . He finds that this band is very strong in ice, lacking in water-vapour, present but weak in water and much reduced in a concentrated solution of NH_4Cl . The cause is ascribed to changing quantities of the species $(\text{H}_2\text{O})_n$, as in Collins' examination.

These two attempts form the only evidence we have of the behaviour of a system in the three physical states. The inference would seem to be that association into heavier units can give rise to an electric moment non-existent in simpler groups.

Organic Compounds

Ellis(9) has described an ingenious automatic recorder for use in infra-red spectral work, and has applied it to the investigation of forty liquids, hydrocarbons, aliphatic halides and organic oils. He used thicknesses varying from a thin film to 10 cms., and found a persistent series of bands at 0.76 , 0.83 , 1.03 , 1.19 , 1.38 , 1.7 and 2.3μ which he has ascribed to the characteristic oscillation of the C—H linkage, and which he suggests may be the 2nd to 8th harmonics of an intense absorption noted by Coblentz at 6.9μ , and of which the first harmonic has long been known at $3.4\mu^*$. Consistent values for the fundamental are obtained if the frequencies are expressed in the form $\nu = n\nu_0(1 - nx)$, where n is a small correction term such as Kratzer has used in his analysis of gas spectra.

This use of the Kratzer correction for liquids is interesting, and probably on the right lines inasmuch as the forces acting are

* Salant suggests from other evidence that the fundamental is 3.4μ not 6.9μ .

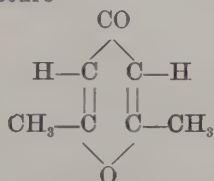
assuredly anharmonic in character. Two difficulties however present themselves in accepting these results whole-heartedly: firstly, it is not likely that an 8th harmonic (or even earlier high harmonics) would have an intensity capable of measurement; and secondly, in liquids, the bands are usually so broad that the corrections may merely be the amount of experimental error, either in observing such feeble intensities or directly due to differences in calibration. This latter possibility of error in calibration is more dangerous than it might appear. If under experimental conditions different from those obtaining in work on a fundamental, the bands designated "overtones" are investigated, then a discrepancy in wave-length scale in the two cases may well give a displacement all in one direction, such as would give rise to a suspected Kratzer correction. Naturally, it is not suggested that this is the state of affairs for this particular series of bands. Yet it is often difficult to record a fundamental frequency under the same experimental conditions as its supposed overtones: for instance, it may lie in a region only accessible with a different prism or grating. The beautiful sharpness under extreme dispersion, of bands in gases, or in solids, is sadly lacking in liquids, and this greatly intensifies the difficulty of obtaining accurate wave-length data.

Another interesting example of work on a set of related compounds is that due to Smith and Boord⁽¹⁰⁾ who studied the spectra in the near infra-red (1.0μ to 2.5μ) of a series of ethers, esters, and related substances. Very little shift seems to occur with molecular structure, but it appears fairly certain that a number of bands found in this region can be attributed to the C—H linkage, and that they form a roughly harmonic series.

A large amount of data on organic liquids has been collected by Bonino (various papers, twelve in all, in the *Gazz. Chem. Italia*, 1923—onwards). It is not profitable to include it here, for it is semi-empirical in character, and leads to little of physical significance. He attempts to incorporate the Bohr-Sommerfeld quantum conditions into the theory of fluids, a venture which, in the present

state of knowledge of the dynamics appropriate to the liquid phase, can hardly hope to be successful.

Ross(11) desires to see investigations upon infra-red spectra of liquids a routine method in organic chemistry. This possibility need not be discussed here, but it is interesting to notice that, in conjunction with Henri's work, there appears to be evidence in favour of the presence of a benzene nucleus and a hydroxyl group in the pyrone molecule. Ross has observed the infra-red spectrum of this compound, and notices that the molecular refractivity R does not agree with the structure



for which R should be 33.3, whereas R is found to be between 34 and 35. Quantitative results are at present too difficult to obtain.

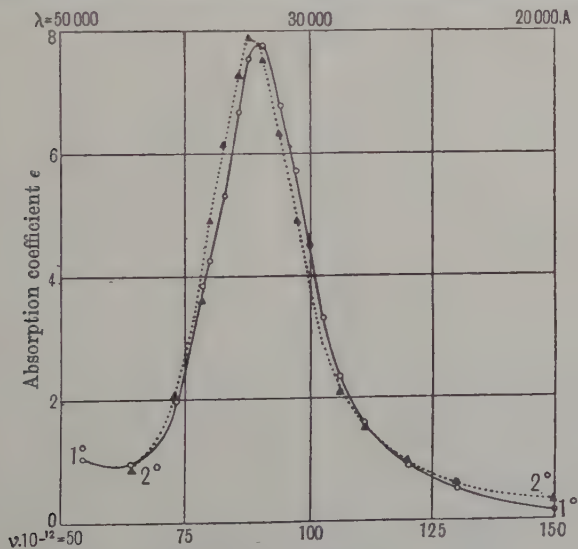


Fig. 11. Absorption of ethyl alcohol (Henri).
Calculated values—dotted line; observed values—continuous line.

Victor Henri(12) has investigated the absorption spectrum of ethyl alcohol, and finds a number of bands which form approximately a harmonic series. This is not convincing, for some members of the series are extremely weak, others very strong, while a number of further bands fail to fit into the scheme at all.

An interesting point, however, is the attempt to compare for this substance the coefficient of absorption ϵ as found experimentally with that calculated from the Ketteler-Helmholtz formula.

Fig. 11 gives a comparison of the two curves and the following table shows the order of accuracy attained.

λ	$\epsilon_{\text{cal.}}$	$\epsilon_{\text{obs.}}$
4.7 μ	0.91	0.96
4.1	2.12	1.96
3.8	3.65	3.81
3.7	4.98	4.25
3.6	6.19	5.33
3.5	7.27	6.66
3.4	7.87	7.57
3.3	7.51	7.75
3.2	6.37	6.78
3.1	4.93	5.72
2.8	2.10	2.37
2.7	1.63	1.64
2.5	0.99	0.90
2.3	0.62	0.54
2.0	0.34	0.17

The work of Marton(13) and a recent extension of it by Gapon(14) show a striving towards theoretical foundations which is welcome. Unfortunately, it is difficult to accept the conclusions reached by these investigators in some particulars; nevertheless, it is something of an advance.

Marton examined hexane, cyclohexane, benzene, aliphatic aldehydes, acetene, chloroform, phosgene and thiophosgene, in the near infra-red, by means of the usual spectroscopic arrangements. He claims a maximal wave-length accuracy of 0.02 μ . This is hard to

credit, since it appears that his datum line was the emission band from a Bunsen burner at about 4.40μ ; this band is known to be quite diffuse. He finds, as is usual, great trouble in obtaining trustworthy reproducibility: thus for the 3μ band in benzene he obtains intensity ratios 0.593, 0.572, 0.592 in three consecutive readings. Like Coblentz he uses a density of readings which is decidedly low.

He comes to the following main conclusions:

(i) A closed ring seems to displace a characteristic band towards longer wave-lengths, and to increase the intensity of absorption.

(ii) Homologous compounds differ mainly in the intensities they show, the shift being exceedingly small. (This is in agreement with other work previously noticed.)

(iii) Unsaturated compounds tend to exhibit bands at shorter wave-lengths than similar compounds lacking the double bond.

(iv) It is possible to construct a series which is harmonic, except for a Kratzer correction.

Gapon's paper is mainly concerned with the expression

$$\nu_i = \nu_c \sqrt{n},$$

where ν_i is the observed wave-number of a line, n is a whole number, and ν_c a characteristic magnitude (of the nature of a wave-number) for each compound.

A table is compiled in the following way:

Taking $n = 1$ fixes ν_c , if simultaneously the lowest value of a set of readings ν_i is chosen. Naturally, this in effect assumes that such a lowest value of ν_i really represents a fundamental for the particular substance, and this is the weak point in the proceeding.

With ν_c thus obtained and also various integral values of n assumed, fair agreement between observed and calculated wave-numbers is found. It is noteworthy from the table (*loc. cit.*) that systematic deviations are occurring, as would be expected, i.e. the differences show either a general tendency to be all of one sign or

the other, for particular compounds, a state of affairs not likely to arise from errors of calibration. This method really amounts to a totally empirical determination of the quantity ν_c .

The next step is to try to obtain an expression for ν_c having some theoretical justification, and with this the second part of Gapon's paper is concerned.

He assumed that the molecules perform "a certain rotational motion about the centre of equilibrium" (exact literal translation from the German), with a velocity u given by

$$u = 2\pi\nu r,$$

where r is the radius of the orbit and ν the frequency.

It is next supposed that the liquids considered shall be in corresponding states, so that the kinetic energy is proportional to the corresponding temperature $T_{\text{corr.}}$,

$$\frac{1}{2}mu^2 = \text{const. } T_{\text{corr.}},$$

from which $m\nu^2 r^2 = \text{const. } T_{\text{corr.}}$.

If P is the internal pressure of the liquid and $V_{\text{corr.}}$ the molecular volume, then according to Stefan

$$PV_{\text{corr.}} = \text{const. } T_{\text{corr.}},$$

so that

$$m\nu^2 r^2 = PV_{\text{corr.}}$$

Next, if α is the coefficient of expansion and $\beta_{\text{corr.}}$ the compressibility in the corresponding state, thus

$$P = \frac{\alpha T_{\text{corr.}}}{\beta_{\text{corr.}}},$$

then

$$m\nu^2 r^2 = \text{const. } \frac{V_{\text{corr.}}}{\beta_{\text{corr.}}}.$$

Taking $\frac{M}{N} = m$ (M = molecular wt., N = Avogadro's number) and $r \propto (V_{\text{corr.}})^{\frac{1}{3}}$ gives

$$\nu_c = \text{const. } \sqrt{\frac{V_{\text{corr.}}^{\frac{1}{3}}}{M\beta_{\text{corr.}}}}.$$

or, taking V and M for like temperatures and evaluating the constant*,

$$\nu_c = 0.34 \times 10^{12} \sqrt{\frac{V^{\frac{1}{3}}}{M\beta}}.$$

A table, with which the paper concludes, gives a comparison between observed and calculated values of ν_c . The agreement in one or two instances is surprisingly good, in others as much as 10% astray.

Nevertheless, the basis of Gapon's argument is obscure, as the following single consideration will show.

ν_c is the frequency of the assumed rotational motion: yet a glance at the tables shows that this corresponds to a wave-length of the order 3μ .

It is hardly conceivable that a rotational motion should give rise to characteristic wave-lengths in this part of the spectrum: it would be natural to expect them to occur at wave-lengths between ten and a hundred times greater.

Liquids and their Vapours

Within recent years Purvis(15) has made a study of the benzene absorption around 3.5μ . He reports that this is a broad structureless region in the liquid spectrum, but that it breaks up into a number of subsidiary maxima in the spectrum of the vapour phase. Unfortunately the equipment was insufficient to establish with certainty any shift in the frequency between the two phases. The mono-derivatives C_6H_5Cl , C_6H_5Br , C_6H_5I in the neighbourhood of 2μ show a complicated structure.

Some later experiments are due to Dreisch(16) who also worked at the 3μ band and below, for water, benzene and chloroform. A calculation of absorption coefficients shows that while at first the vapour absorbs more strongly than the liquid, the reverse is the

* From a careful analysis of a similar problem by Braunbek (*Z. für P.* 38, 549, 1926), it seems likely that the constant is really a complicated function of M .

case from 1.5μ to 2.0μ . He confirms the very small magnitude of the shift in wave-length for the same absorption band between the liquid and vapour phases.

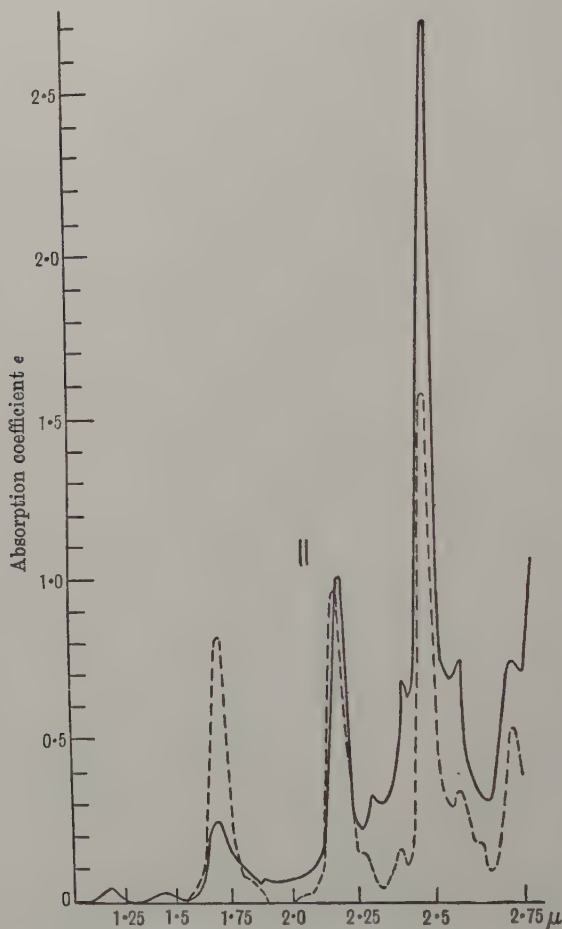


Fig. 12. Absorption of liquid (continuous line) and vaporous (dotted line) benzene (Dreisch).

In general, it seems that the liquid band appears at the higher wave-length.

(2) *Solutions*

Some characteristic results and their implications from a study of infra-red absorption in solutions are now considered. The first example is that where the solute is a gas, and the second in which it is a salt.

Daniels(17) has examined the bands from N_2O_5 dissolved in the following solvents: carbon tetrachloride, chloroform, dichloro-ether, tetrachloro-ethane, carbon disulphide, nitromethane, isopropyl bromide, butyl ether.

No shift is recorded for N_2O_5 from solvent to solvent. This is of some consequence in the light of the radiation hypothesis put forward by Perrin(24) and W. McC. C. Lewis. According to this, the temperature coefficient of the velocity of a reaction should enable a calculation to be made of the effective radiation which is supposed to cause it. Such a view demands absorption for gaseous N_2O_5 at 1.16μ , which does not occur. Absorption is found however at the multiples 3.3μ and 5.8μ . Should these bands really have a significance in this direction they ought to shift from solvent to solvent according to the different temperature coefficients of decomposition. No shift seems to be present, though Daniels is of the opinion that he could detect a shift of 0.05μ . This is not very sensitive, but one would expect the shift to be as great as this if it existed.

Reinkober(18) has published the data obtained from careful work on the absorption spectra of water, alcohols, and a concentrated solution of NH_4Cl between 2μ and 9.5μ .

This author has also investigated solid NH_4Cl , and found that these short infra-red oscillations, due to vibrations taking place within the NH_4 group, occur at shorter wave-lengths in solutions than they do in the solid. This is the opposite of the effect usually found, but then it is to be remembered that NH_4 is the positive ion in this salt, whereas it is usually the behaviour of the acid groups which is considered in the transition solid \rightarrow solution.

Fajans(5) has pointed out that this effect agrees with his theory of the absence of molecules in solutions of strong electrolytes.

Another point brought out by Reinkober is that for the prominent NH_4 band near 7.0μ no displacement beyond a few hundredths of a μ was found when NH_4Cl was investigated in five different solvents, a result in accord with that of Daniels just described.

There seems little doubt that the "solvent-gathering power" of ions, in its relation to dielectric constants and positions of characteristic infra-red absorption, is a matter of much complexity.

(3) *Solid Solutions*

As a justification of the position of this subject here, it may be well to give a few points of present-day knowledge upon solid solutions. There has been a change in the way in which they are regarded, largely as a result of researches by X-rays, and also because of the importance of glasses and other amorphous complexes in industry.

Solid solutions were, apart from a few minor examples, originally of interest to metallurgists and petrographers, who took great care in establishing "diagrams of thermal equilibrium," that is expressing the freezing-points of such aggregates as a function of the atomic concentration. From this method of investigation arose a scheme of classification. Pairs of metals were found to form unbroken series of mixed crystals with one another; the series in some cases lasted throughout the whole range of concentrations, but sometimes produced eutectics near one end. In the same way, elements and oxides were shown to be capable of remaining dissolved in the glassy products of an igneous magma. This is the origin of a number of gem stones. In each of these cases, all microscopical examination revealed only the apparently unaltered solvent. There is thus a close analogy to the behaviour of liquid solutions.

X-rays however have lately shown a number of interesting points in alloys and glasses, but such results may be ignored as irrelevant to the present treatment. The basic fact remains that these amorphous phases can often be considered supercooled liquids.

It should now be clear that sharply defined characteristic frequencies are not likely in the spectra of these substances; wide regions of absorption and transparency seem more probable. Investigation of the general position of such diffuse bands may well be an important part of infra-red work, for, compared with their great extension on a frequency scale, the limits of the bands are defined with fair accuracy. Such work does not require elaborate experimental arrangements; it is often sufficient to know with reasonable certainty the percentage transmission of specimens of standard thickness between given wave-length limits. A number of glasses, coloured and otherwise, have been examined in this way by Coblenz, and he obtained results which provide convenient guides in the selection of material for optical instruments.

Thus, a common microscope cover-slip of thickness 0.09 mm. showed absorptions at 5.5μ and 6.25μ which correspond fairly closely with well-known bands of SiO_2 .

Again, a specimen of glass only 0.001 mm. in thickness showed a transparency of 90% up to 8μ . This affords an interesting comparison with the behaviour of glass of "ordinary" thickness, i.e. that of electric lamp bulbs, which is usually opaque to infra-red radiations well on the shorter wave-length side of 3μ . With the very thin piece, Coblenz examined the reflection spectrum, and found a number of considerable maxima near 9μ . When the composition of the melt was altered the intensity varied a good deal, but little effect was recorded upon the positions of the bands. This appears to be in general agreement with what is found for ordinary liquid solutions, in which concentration seems to have little influence on band displacement.

A number of emission spectra of typical glasses may also be mentioned. A soft glass, drawn out into a solid rod, gave lines at $2.0, 2.86, 3.6, 4.4, 5.5\mu$ which may be compared with the emission spectrum of SiO_2 .

On the other hand, Schott's blue-violet glass absorbs strongly

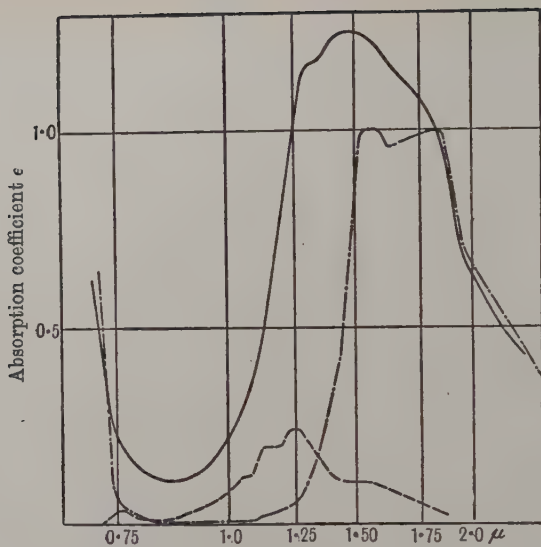


Fig. 13. — cobalt glass.
 - · - CoCl_2 dissolved in HCl.
 - - - CoCl_2 dissolved in water.
 (Dreisch.)

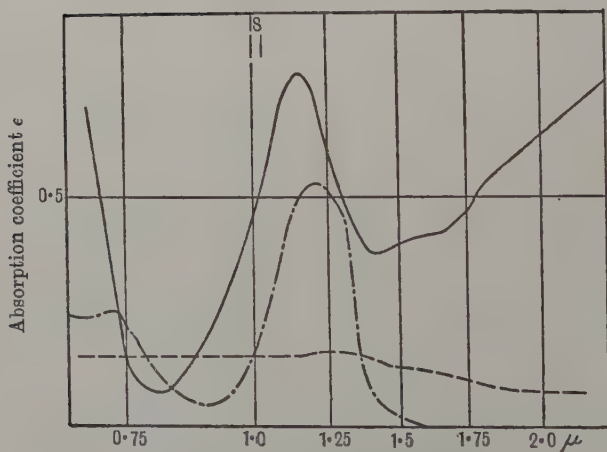


Fig. 14. — violet nickel glass.
 - · - yellow nickel glass.
 - - - NiCl_2 .
 (Dreisch.)

between 0.5μ and 2.0μ . This was used by Ångström in his investigations on solar violet radiation. This glass, with a water cell 1 cm. thick, absorbed all radiation beyond 0.5μ .

Evidence was also forthcoming that ruby glass probably contains copper or gold in the colloidal state.

According to Coblentz, it is possible to classify glasses into two groups: (1) those having a strong absorption in the visible or in the infra-red, and (2) those possessing a wide region of absorption in the visible, the transparency increasing with wave-length (i.e. towards the infra-red).

Examples of the class (1) are cobalt glass and the Schott blue-violet variety already mentioned, whereas (2) includes the red glasses, which partake more of the nature of a turbid medium, in which colour is due to metals in a fine spherical state of distribution.

Dreisch(19) has also worked on the question of metallic salts dissolved in fluids and in glasses. It appears from his results that the absorption spectrum is similar in both cases.

(4) *Water of Crystallization*

It is common knowledge that many salts crystallize with a number of molecules of water of crystallization.

A consideration of the effect of this upon infra-red spectra will be undertaken here rather than in the chapter on solids, for it is not of great interest for the main theme of that section.

Now there are characteristic bands due to water in the near infra-red at the following wave-lengths (approximately)

3.2μ

6.3μ

19.5μ

corresponding to portions of the spectrum usually investigated with prisms of quartz, fluorspar or rock-salt, sylvine, and it is within these limits that most of the characteristic internal oscillations in acid radicles are to be found. Experiment shows that these marked

water bands are retained with slight modifications in a crystal containing water of crystallization.

What exactly the relation of the water groups to the radicle groups may be is an interesting though obscure question, but Schaefer⁽²⁰⁾ has pointed out that this water of crystallization possesses a kind of mimicry, in the sense that it becomes uni-axial in uni-axial crystals, and bi-axial in bi-axial ones: in other words it appears to assume the optical character of its surroundings. A detail which has not up to the present been settled is the relationship of the intensity of these water bands to the number of molecules of water of crystallization present.

An interesting case for research would be that of copper sulphate, which at different temperatures holds different numbers of molecules of water of crystallization.

The difficulty of having, in addition to the necessities of infra-red spectroscopy, a means for the accurate control of temperature, has tended perhaps more than most things to retard progress in such directions as these.

Schaefer also remarks that water in a state of combination with amorphous substances shows decidedly less distinct bands, and this suggests the gradual transition between liquid and solid already hinted at in the last section.

The mineral group known as zeolites is usually supposed to contain water of crystallization: these bodies are certainly completely crystalline, yet the water bands are very weak. Apparently this is a less "rigid" connection than usual between the water groups and the mineral lattice.

(5) *Liquid Crystals*

It has for many years been known that some liquids possess the property of becoming bi-refrangent if stirred from a state of rest. In addition to this optical peculiarity, the mechanics of such systems appear interesting. If a quantity of such a liquid is given a rotational

motion in one direction, say clockwise, then when it comes to rest, as it does very soon, since the viscosity is always high, there is an appearance of unwinding in the reverse direction (anti-clockwise). Liquids which show this bi-refringence to any extent as proved by examination with a pair of Nicols are sometimes called liquid crystals, and there is no doubt that they represent a frontier between crystals and ordinary isotropic liquids. The high viscosity also points to this transitional nature. This is an open field for the investigator in the infra-red. From what has just been said it is clear that absorption spectra would need to be observed in polarized radiation. This is not exactly an easy matter, but by no means an impossible one. The unfortunate fact is that most substances displaying properties of this kind are chemically and physically very complicated.

The nearest approach to information existing on this subject is provided by an X-ray examination by Lingén, who finds that the organic substance *p*-azoxyanisole shows no change of structure in the rigid or plastic varieties.

A preliminary attempt in the infra-red shows no difference of spectra of the solid, anisotropic liquid (i.e. liquid crystal) or liquid states.

Kast(21) has recently examined this peculiar anisotropic melt of the substance *p*-azoxyanisole from a magnetic standpoint. He finds the astounding result that its magnetic moment is no less than 9.43×10^{-17} c.g.s. (about 10^4 Bohr magnetons), which suggests a structure of great complexity.

Erréra(22), from evidence upon the variation of the dielectric constant of this substance with temperature and frequency of impressed field, has been led to the surmise that, near the melting-point, a colloidal state exists, perhaps as plastic layers in between portions of a truly solid phase.

This being so, it is hardly reasonable to expect any clear-cut issues from mapping the positions of bands of such an involved assemblage. Further work on the infra-red spectra of compounds like

p-azoxyanisole might, if carried out with polarized radiation, throw light on the crystalline properties of anisotropic melts.

(6) Magnetic Rotation

In recent years there has been a revival of interest in the magnetic properties of elements and salts, mainly because of the more definite views given by Bohr and his followers to the physical inter-

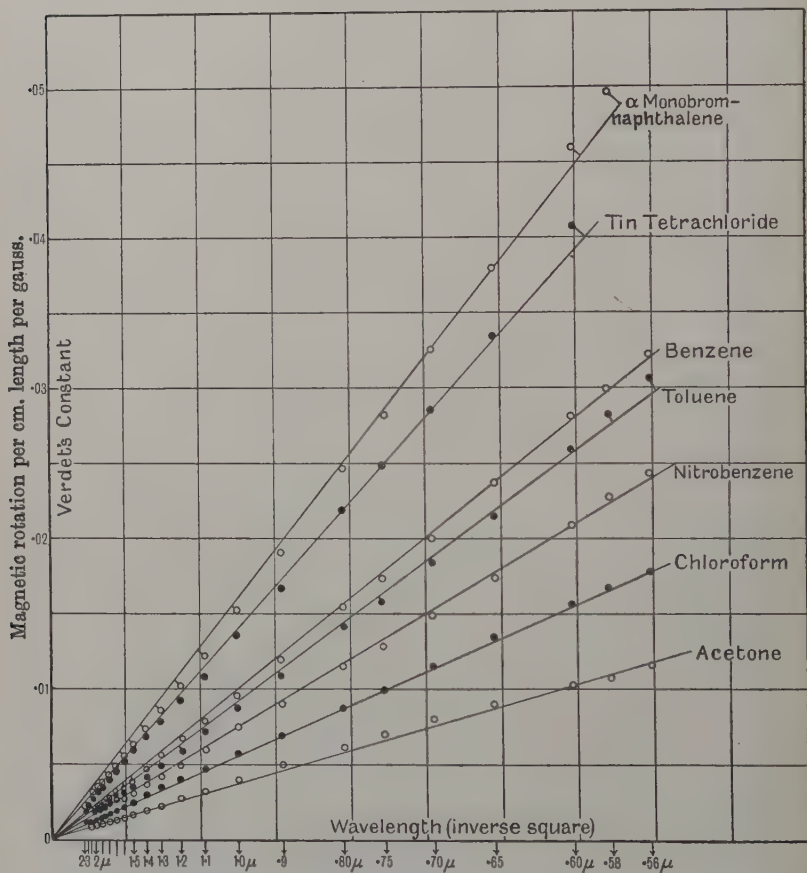


Fig. 15. Positive magnetic rotations of various liquids in the infra-red. Wavelengths are indicated in microns (Ingersoll).

pretations of the Periodic System of the elements. At the same time, technique for the attainment of magnetic fields of great intensity has been steadily improving, as well as the accuracy with which a field of required strength can be brought into action.

As in the visible, there is no doubt that a definite relationship exists between the wave-length and the magnetic rotation for a given liquid, or class of liquids.

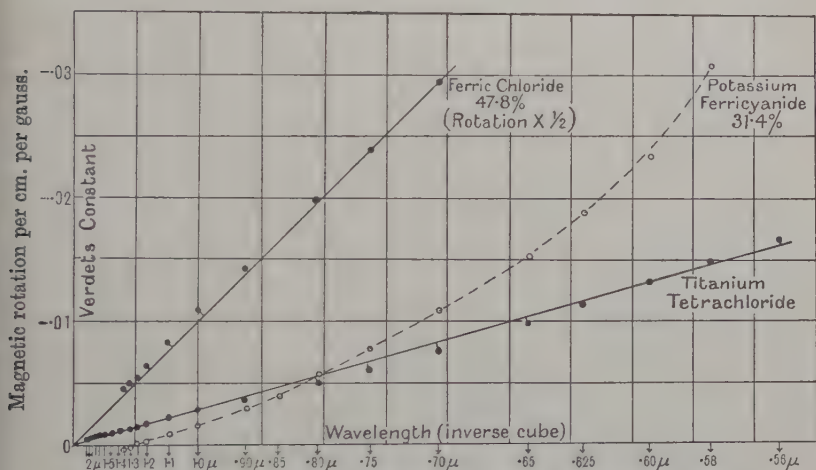


Fig. 16. Negative magnetic rotations of different solutions (Ingersoll).

Ingersoll(23) has made, within the range of wave-lengths 0.56μ to 2.3μ , a systematic investigation of the magnetic rotation and the index of refraction of twenty pure liquids and as many aqueous solutions of metallic salts. It is unfortunate that it has not so far proved feasible to go to longer wave-lengths, for regions of intense characteristic bands set in for many liquids and solutions between 3μ and 4μ .

Within this limited range it is found that positively rotating liquids yield a rotation which is very nearly proportional to the inverse square of the wave-length. This indicates that infra-red absorption bands, in this particular portion of the spectrum, exert little influence on the rotation.

A much increased rotation dispersion is shown by negatively rotating liquids, of which however there are comparatively few.

Titanium tetrachloride, the only diamagnetic substance yet known to show negative rotation, and also concentrated ferric chloride solution show a magnetic rotation nearly proportional to the inverse cube of the wave-length; potassium ferricyanide shows a rotation varying with the inverse fifth power.

The $\frac{l}{m}$ ratio calculated for positive liquids shows, in general, a decrease for the longer wave-lengths.

Vaporization of Liquids

Perrin(24) quantizes the act of vaporization, supposing that the latent heat of vaporization is provided by the absorption of energy for radiation of a particular frequency ν . This at once leads to $L_i = Nh\nu$, where L_i is the internal latent heat, N is Avogadro's number and h Planck's constant. This should mean that a liquid will possess a band of absorption around ν , which band must be absent in the vapour spectrum. It does not seem at present clear that such a condition is always fulfilled, but it may be noted that since L_i may be written as equal to $L - RT$, where L is the observed latent heat and RT is the work done against external pressure, then

$$\nu = \frac{L - RT}{Nh};$$

and because Trouton's rule states that L is proportional to the boiling-point it therefore follows that the frequency ν which is responsible for vaporization is directly proportional to the absolute boiling-point.

This assumption of a single frequency of activation is not a very plausible one, since the radiation which is in equilibrium with the liquid has an energy distribution given by Planck's radiation law, and at the best a very large range of frequencies must be present in considerable intensity. Rideal(25) points out however that the

maximum intensity lies at a frequency ν given by Wien's displacement law,

$$\nu_{\max} = T \times \text{constant},$$

and this is exactly the form of the expression given above for ν .

If therefore the frequency ν_{\max} as given by Wien's law be supposed to be the one chiefly responsible for the act of vaporization, it follows at once that at the boiling-point T_b

$$Nh\nu_{\max} \doteq L_i$$

or $\frac{L_i}{T_b} \doteq \text{constant}$, which is one form of Trouton's rule.

However it may be assumed that at the critical temperature T_c all the molecules are equally activated in their capacity for vaporization, since at the critical temperature the latent heat is zero. In other words, the energy distribution in the radiation in equilibrium with the liquid at temperature T_c is exactly that sufficient to activate all the molecules so as to cause vaporization. Hence L_i may be more accurately given by $L_i = Nh\nu_{\max}$ at the critical temperature,

or $\frac{L_i}{T_c} = \text{constant}^*$. This is the best form of Trouton's rule,

and moreover since Wien's constant is known the constant in Trouton's rule may be calculated, and the value so obtained, 9.866, is the mean of that obtained by experiment and that given by van der Waals' equation.

Rice has obtained the equation $E + kT = h\nu$, where E is the critical increment per gram-molecule, and N the number of molecules in one gram-molecule.

In general, the abbreviated form $E/N = h\nu$ is sufficient, in which E/N is the amount of energy which must be added to decompose a single molecule.

Some experimental evidence about the validity of this expression is due to von Halban (26), who has studied the process of decomposition of triethylsulphonium bromide into ethyl bromide and diethylsulphide in various solvents (the reaction is unimolecular).

* T_b is approximately equal to $\frac{2}{3}T_c$.

If it is assumed that one quantum per molecule is needed, it is possible to arrive at a value for the frequency ν and to compare the result with observations in the infra-red (27).

Substance	Critical increment	Wave-length (calc.)	Wave-length (obs.)
Nitrobenzene	28,390 cal.	1.0 μ	0.95 μ
Tetrachloroethane	31,030 "	0.91	0.90
Propyl alcohol	33,960 "	0.84	0.89
Amyl alcohol	33,530 "	0.85	0.83
Benzyl alcohol	36,180 "	0.78	0.80
Acetic acid	29,220 "	0.97	0.93

For acetone and chloroform the figures are discrepant. von Halban considers, from the abnormal course of his velocity constants, that in the former case ionization has set in, and in the latter polymerization.

Work along similar lines has been published for sucrose by Moran and Taylor (28) and for maleic acid by Höjendahl (29).

A recent discovery by Raman (30) may prove the starting-point for a much more accurate mapping of the infra-red absorption bands in liquids than has hitherto been possible. When, for example, benzene is irradiated with the mercury line 4358 Å. and the scattered light is analysed with a spectrometer a number of lines of modified frequency appear. Careful measurement shows that the frequency differences between the incident and scattered lines are exactly equal to characteristic infra-red frequencies of the molecule, and thus correspond to absorption of energy. Most of the modified lines are of longer wave-length than 4358 Å., but for benzene two lines of shorter wave-length than 4358 Å. can also be seen, indicating a negative absorption of radiation.

Such a phenomenon as negative absorption plays an important part in the Kramers-Heisenberg dispersion theory, and therefore a definite proof of its existence is of interest.

The method is capable of great precision. For example, its application to carbon tetrachloride leads to the knowledge of a doublet at 12.6μ and 13.0μ , and this is in excellent agreement with the fact that a broad unresolved band with its centre near 13μ was observed by Coblentz twenty years ago.

CONCLUSION

While most of the work done on liquids has a qualitative value, its importance as a definite contribution to knowledge is impaired by its lack of theoretical foundation. Even with this drawback there seems no limit to the mass of empirical material produced.

A use for the data is suggested by the potentialities of infra-red research upon glasses and other amorphous melts of industrial value.

The comparatively low order of experimental technique required allows here, more than anywhere else, an approach to routine conditions; and the same might apply in the very near infra-red below 1μ , to determinations of transmissions in gelatine filters and other products coming increasingly into favour in long-wave photography.

Theoretical considerations, except in a more or less crude form, hardly touch this sphere of investigation, and there is certainly no reason why infra-red investigations should not find a use in semi-empirical ways in industry.

Nevertheless, in some directions there is the possibility of a theoretical basis. Thus observations upon solutions are capable of "explanation," if only to a limited extent, in terms of a generalized theory of electrolytic conductivity resting essentially upon Gibbs' phase integral. The solution is either by way of the virial, or the analysis of Debye and Hückel, if the former method is too difficult. Work upon magnetic rotation also can call upon a theory of dispersion to give it a physical explanation.

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Chapter 3: SOLIDS

Introductory

THE application of infra-red spectrum analysis to the problems which are presented by the solid state of matter is more difficult than is the case with the gaseous phase. This is chiefly because of the greater complexity of the systems of forces involved in the stability of those electrical doublets with which response to electromagnetic stimulus is concerned. At the same time, the problem of the interpretation of infra-red spectral data is more tractable when the material under observation is crystalline than when it is in the liquid or amorphous phase, owing to the orderly nature of the spatial arrangement in the solid state.

Just as X-rays afford a method by which the crystallographer may determine the static condition of the space lattice, so infra-red spectrum analysis yields information from which the relationships governing the dynamic behaviour of the crystal centres may be deduced. Indeed it may be foreseen that from such means of attack a weapon will be forged which not only will be powerful in revealing the secrets of atomic and molecular linkage, but which may enable a check to be imposed upon the accuracy of deductions made from X-ray analysis.

For the present, imperfectly developed methods and a lack of accurate experimental data are hindrances, although in spite of the practical difficulties inherent in work in the infra-red some progress in this direction may already be observed.

In reviewing the achievements which have been made in this branch of infra-red spectroscopy, notice will be taken first of the more general theoretical details in so far as they have been studied and then the experimental work and its interpretation will be broadly surveyed.

General questions of a theoretical nature

The Born-Kármán⁽¹⁾ theory of the solid state has given a picture of the atoms composing a crystal as bound together by a system of forces, essentially electrical in nature, into a regular space lattice of symmetry identical with the macroscopic symmetry of the crystal itself. This lattice may be divided into unit cells, all of which are similar, and which contain s particles each, of which p are atoms, the remainder being electrons.

It may be shown that in general, for an isotropic crystal, the total number of different frequencies of vibration possible to the particles in this unit cell is given by $3s$, of which $3(s - p)$ are electronic and consequently appear in the ultra-violet, $3(p - 1)$ are due to the atoms, and 3 are purely acoustic or elastic, associated with the body of the crystal as a whole. With the last two types this survey need only be concerned.

As may be expected, if the order of the symmetry of the lattice be raised, some of these frequencies become numerically equal, and the total number of different atomic frequencies becomes $2(p - 1)$ for uni-axial and $(p - 1)$ for regular crystals, the acoustic frequencies suffering a corresponding reduction in their number. These acoustic terms may be regarded as the upper limit of frequency of elastic waves which can be propagated through the crystal in the particular direction considered, and this limit must depend solely upon the atomic spacing and the forces which keep the atoms in equilibrium. If the crystal vibrates like a rod, there is present, in addition to the simplest mode, a whole range of overtones, to which series a limit is set when the wave-length in the crystal becomes identical with the linear dimensions of the unit cell. In other words, the acoustic frequency forms the upper limit of integration in the Debye expression for the specific heat, and will be referred to later in this chapter.

Active and inactive oscillations

In general, the $3(p - 1)$ atomic frequencies may effect the passage of electromagnetic radiation, because if any of the p atoms are ionized,

or indeed if they possess any electric charge, or even if they contain an electric doublet set up by deformation of the electronic shell, then the frequencies associated with these atoms can be stimulated by an impressed field of suitable period.

Such a state will make itself evident by an absorption of the energy, or if the resonance is sufficiently marked by reflection, and by dispersion of a continuous spectrum. Such frequencies are called "active," while those which are due to the vibration of electrically neutral atoms are called "inactive" and cannot be observed by optical means.

Prediction of type of frequency from symmetry considerations

In some cases it is possible to examine the symmetry conditions in detail, and not only to fix the number of possible vibrations, but also to ascribe particular frequencies to particular modes of motion of the particles within the unit cell.

Brester(2) has examined the structure of calcite, purely from a crystallographic aspect, and has shown that there are active frequencies to be expected in the long wave-length region of the infra-red, due to the mutual swingings of the calcium ions and the CO_3 groups; four frequencies, one of which is inactive, arise from oscillations within the CO_3 group; and also frequencies which would fall in the long wave-length part of the spectrum were they not inactive. These last, being due to mutual swinging of similarly charged ions, do not involve any alteration in electric moment. All the active frequencies have been observed, and Brester concludes therefore that the agreement is satisfactory between theory and experiment.

The specific heat of a crystal

To return to a consideration of the $3s$ frequencies which can occur in a unit cell of s centres, it is clear that the vibrational energy of such a cell would be obtained by summing the energy distributed according to quantum laws among all the vibrations.

The energy at a temperature T of a linear vibrator of frequency ν is given by

$$U = \frac{h\nu}{(e^{\frac{h\nu}{kT}} - 1)},$$

i.e. the specific heat of such a cell would be given by

$$\frac{\partial}{\partial T} \sum_0^{3s} U = \sum_0^{3s} \frac{kx^2 e^x}{(e^x - 1)^2}, \text{ where } x = \frac{h\nu}{kT}.$$

(h and k are Planck's and Boltzmann's constants respectively.)

It is obvious that at ordinary temperatures the energy in the $3(s-p)$ electronic vibrations will be negligible owing to the high values of ν , and the specific heat will be satisfactorily represented by the summation between the limits 0 and $3p$.

When the summation is extended over a large number of such unit cells so as to include one gram-atom of the crystal, new elastic frequencies make their appearance, owing to the increased number of degrees of freedom of the solid considered as a whole; in fact the three acoustic frequencies are each replaced by the elastic spectrum of Debye, so that $3(p-1)$ terms are left under the summation sign, and three new Debye terms replace the three simple expressions for each of the elastic frequencies.

The complete expression (3) for the specific heat of a crystal is given by

$$C_v = \frac{N}{3p} \left\{ \sum_{\nu_1}^{\nu_3} D(x) + \sum_{\nu_4}^{\nu_{3p}} E(x) \right\},$$

where $E(x)$ is $\frac{kx^2 e^x}{(e^x - 1)^2}$, and $D(x)$ is Debye's function and N is Avogadro's number ($= 6.06 \times 10^{23}$).

Heats of Formation, Fusion, Sublimation, etc.

Not only are the vibrations of a solid the determining factors in the expression for its specific heat, but they affect in addition various thermochemical constants. Haber(4) and W. McC. C. Lewis(5) have shown that the heat of formation Q of a compound may be

expressed in terms of characteristic frequencies associated with the reactants and the resultants. Their expression is

$$Q = \sum N h \nu_{\text{reactants}} - \sum N h \nu_{\text{resultants}}.$$

The treatment identifies the ν 's with the optically active frequencies found throughout the electromagnetic spectrum, and in some cases the heats of formation of materials are given by the insertion into the above equation of appropriate values for ν obtained from spectroscopic data. In the chapter on liquids some work of von Halban (6) and others is described, but as most of the heats of formation actually met with in practice are so large that they must more often be attributed to frequencies lying in the ultra-violet region, it is not necessary to make further reference to the subject here.

Perrin (7), in an essay on the inter-relationships of matter and light, has attempted to correlate a varied assortment of phenomena with quantum absorption of radiation. Amongst his suggestions may be noted the idea that the processes of change of physical state, fusion or sublimation, and vaporization, are caused by absorption of radiation of a definite frequency in a manner precisely similar to photochemical processes, and governed by the same law of photochemical equivalence, enunciated by Einstein. That is to say, each gram-atom which undergoes change of state and in so doing absorbs heat energy L is supposed to obtain that energy by absorption of N quanta of radiation of frequency ν , so that

$$L = N h \nu.$$

Perrin supposes the two processes involved, fusion and crystallization, or vaporization and condensation, each to be photochemical, the one absorbing radiation of frequency ν , the other radiation of frequency ν' , so that the equation becomes

$$L = N h (\nu - \nu').$$

This most ingeniously accounts, at any rate qualitatively, for the existence of a maximum speed of crystallization of supercooled liquids at a particular degree of supercooling. Using that fact

Perrin obtains a value for the ratio $\frac{\nu}{\nu'}$ and calculates two examples,

benzophenone and sulphur. The wave-length of radiation responsible for fusion he finds to be 3.4μ in the case of benzophenone and 3.7μ in the case of sulphur.

How much or how little lies behind this hypothesis it is difficult to say, but it may be noticed that the first consequence of it would be that change of state should be accompanied by the disappearance of those absorption bands corresponding to the particular frequency ν concerned, and by the appearance of others corresponding to ν' , the frequency activating the reverse change. This is not at present known with sufficient accuracy for a crucial decision to be made in the case of such a substance as H_2O , which in both liquid and vaporous states has a very complex spectrum. The subject has been referred to in the chapter on liquids, but it may be remarked that Taylor and Rideal(8) have found that liquid, supercooled, and solid sulphur, both rhombic and prismatic forms, all possess substantially identical spectra from 1μ to 15μ , and in none does any band appear at 3.7μ .

The regions in the spectra of solids

For convenience in presentation, practical work in the infra-red falls naturally into two main divisions which correspond approximately to those governed by differences in observational methods. The first, or long wave-length category, includes only those frequencies of vibrations characteristic of the band between the acidic and basic groups, whereas the second is mainly concerned with the so-called internal oscillations of compound radicles.

The long wave-length region, $\lambda > 30\mu$

In this region is included both "active" and "inactive" oscillations, and although the infra-red spectrum as such is only concerned with the former, yet from what has already been said, the inactive vibration may assume considerable importance. In addition to the optical methods by which the characteristic vibrations may be determined, various theoretical formulae of wider application will be discussed.

Optical methods of finding ν *(a) Drude dispersional frequency*

The existence of a natural period of vibration of the components of electric doublets within a medium leads to an increase of the refractive index of the material concerned according to the well-known Drude theory of dispersion. It is found that the refractive index of simple salts, for instance rock-salt, sylvine, etc., can be accurately represented by a Drude formula having two terms, one involving a natural frequency in the ultra-violet, and the other a lower frequency situated in the far infra-red.

Accurate measurements of the refractive index over a wide range enables the value of these frequencies to be calculated with some precision.

Thus, for example, the Drude equation with two terms is

$$n^2(\lambda) = b^2 + \frac{M_1}{\lambda^2 - \lambda_1^2} + \frac{M_2}{\lambda^2 - \lambda_2^2};$$

when $\lambda \rightarrow \infty$ there follows $n(\infty) \rightarrow b$.

Rubens(9) found the following values for the constants:

Substance	b^2 $= n^2(\infty)$	M_1	M_2	λ_1	λ_2	κ	λ (Havelock)
CaF ₂	6.0104	0.00612093	5099.15	0.0943 μ	35.48 μ	6.8	39.9 μ
NaCl	5.1790	0.018496	8977.0	0.1293 μ	56.12 μ	5.85	61.9 μ
KCl	4.5531	0.0150	10747.0	0.1529 μ	67.21 μ	4.94	72.6 μ

In the last two columns are given the values of κ the specific dielectric capacity and Havelock's values of the wave-length corresponding to the natural frequency, calculated from Reststrahlen. These values are in reasonable agreement with λ_2 , the wave-length of the frequency which occurs in the Drude dispersion formula.

It is also to be noticed that $n^2(\infty)$ is of the same order as κ the dielectric constant. This is in accordance with Maxwell's theory.

Drude's dispersional formula thus provides the first method of finding the characteristic infra-red frequency of a substance. It

must be remembered that the method becomes inapplicable if more than one, or at the most two, natural periods are possible, since the Drude formula becomes unmanageable if the number of terms is unduly increased.

(b) *Reststrahlen or Residual Rays*

The effect of a natural frequency of vibration of the electrical components of a medium is most pronounced when the period of the incident wave is in the neighbourhood of the natural period, and it is easily seen that both absorption and reflection of the

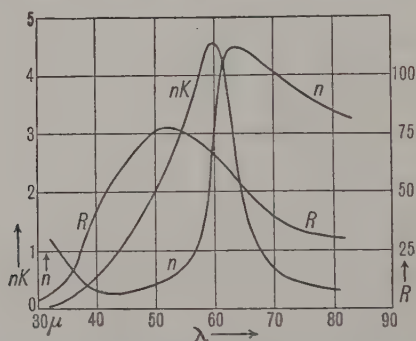


Fig. 17. Reflective power R , refractive index n , and absorption coefficient nK , of rock-salt, plotted as a function of the wave-length λ (Havelock).

wave become appreciable in this region. For waves of period approximating to the natural period the reflective power, absorption, and refractive index of a material possess each a pronounced maximum, but these several maxima do not coincide. The exact relationship between the frequencies at which these quantities attain their greatest value has been studied by Havelock(10), Försterling(11) and others, and Fig. 17 gives curves showing the general aspect of the variation. Havelock derives a formula by which the value ν of the natural frequency may be calculated from ν_R , the wave frequency at which the reflective power R is a maximum.

Experimental measurement of R can thus be used to determine

the characteristic frequency ν . The figure so found for simple salts agrees well with the value obtained from the Drude dispersional formula. It may be noticed that one method of deducing ν_R would entail plotting the reflective power against the frequency, when the value ν_R may be read off from the graph as being the frequency corresponding to R_{\max} . A simplification may be effected by the use of Reststrahlen or residual rays. R is small, except in the neighbourhood of ν_R , and hence if a beam of radiation containing all possible wave-lengths be reflected successively from a number of surfaces of the material under investigation, the result will be the production of a beam in which all frequencies have been so weakened as to be practically extinct, save only for a narrow region immediately surrounding ν_R . Such a beam of radiation of narrow range of wave-lengths may be analysed by a grating without any of the complexity usually introduced into such measurements by the overlapping of spectra.

The earlier work in the infra-red by Rubens(12), Nichols(13), Aschkinass(14), Hollnagel(15) and others almost invariably employed Reststrahlen in some similar manner.

On the question of the inter-relationship of the Reststrahlen frequency and the characteristic frequency of vibration of the lattice, the most recent contribution is that of Fuchs and Wolf(16). Using a Drude dispersion formula and taking the known dispersion of rock-salt and sylvine between 1800 \AA. and 23μ as experimental data they calculate the characteristic frequency ν_i (which corresponds to a wave-length λ_i). The Drude dispersion formula however refers to a frequency ν_i which is to be identified, according to Fuchs and Wolf, with the free vibration of any two oscillating charged particles, and the actual characteristic frequency ν_i' of the crystal as a whole is slower than this because of the inter-coupling of the vibrations, i.e. λ_i' is longer than λ_i . Fuchs is able to calculate λ_i' from the value found for λ_i . There is still the Försterling(11) correction to be applied, for the wave-length at which selective absorption is a minimum, i.e. λ_i , is generally longer than λ_R , that at which selective

reflection is a maximum. This difference may be calculated in one of two ways, but Fuchs arrives at the conclusion that both result in shifting λ_R towards λ_i and away from λ_i' , i.e.

$$\lambda_i < \lambda_R < \lambda_i'.$$

Havelock's method of calculating this correction is formally more correct, and his values of λ_i' calculated from λ_R , as determined by Rubens, agree much more closely with Fuchs' values calculated from λ_i obtained from dispersion, than do those of Försterling.

Theoretical methods of finding ν

To return to the theoretical aspect of infra-red frequencies, it is clearly of importance from a physical point of view that experimental methods are available which can give estimates of the periods of vibration of component parts of the crystal lattice.

These periods must be dependent upon the elastic forces in the crystal, and in fact may be used to verify predictions which can be made from a knowledge of the elastic properties.

Born calculates the optical frequency from his theory of the solid state, employing as data only the dielectric constant and the density of the material. The reader may be referred to the original *Atomtheorie des festen Zustandes*(17) for the elaboration of the calculation, but Born's formula may be deduced in the following simplified manner when salts of the type AX are concerned. The calculation only applies to polar compounds.

If the solid be composed of an array of ions of masses m_1 and m_2 bearing charges $+e$ and $-e$ respectively, it will be obvious that the restoring force on each ion, if the positive and negative lattices so formed are mutually displaced, may be written (provided x is small) as $\frac{x}{\beta}$, where x is the relative displacement and β is a constant.

This assumes that the forces are not anharmonic. The motion

following on any such displacement is represented by $\frac{d^2x}{dt^2} = -\frac{x}{\beta m}$,

where $m = \frac{m_1 m_2}{m_1 + m_2}$ and the frequency of this simple harmonic vibration is

$$\nu = 2\pi \sqrt{\beta m}. \quad \dots\dots\dots(1)$$

If instead of a dynamic displacement the substance be subjected to an electric field of intensity \mathbf{E} , it will suffer a static distortion and the relative displacement of the lattices will be $\beta \mathbf{E} e$. The displacement of charged ions contributes to the dielectric constant, and if ϵ_0 be that portion of the dielectric constant which is caused by polarization of the electronic shells of the atoms (i.e. the constant part which is independent of the frequency of the impressed field), then (if ϵ is the total dielectric constant),

$$\frac{\mathbf{E} \epsilon_0}{4\pi} + n e^2 \beta \mathbf{E} = \frac{\mathbf{E} \epsilon}{4\pi},$$

where n is the number of ions of one sort per unit volume,

or
$$\beta = \frac{\epsilon - \epsilon_0}{4\pi n e^2}. \quad \dots\dots\dots(2)$$

n may be written as $\frac{N\rho}{M_1 + M_2}$, where N is Avogadro's number, ρ is the density, and M_1 and M_2 are given by $M_1 = m_1 N$, $M_2 = m_2 N$.

On writing e as equal to $\frac{Fz}{N}$, where F is the charge carried by 1 gm. atom of hydrogen, and z is the valency of the atoms of the crystal, and as $\lambda = \frac{c}{\nu}$, there finally results, on inserting these values and combining equations (1) and (2), the expression

$$\lambda = \frac{c \sqrt{\pi}}{Fz} \sqrt{\frac{(\epsilon - \epsilon_0) M_1 M_2}{\rho}},$$

which is the formula deduced by Born for polar compounds of the type AX . A slight modification will make the formula applicable to substances of the type AX_2 .

The following table shows the results obtained with several typical crystalline salts.

	$(\epsilon - \epsilon_0)$	ρ	λ
NaCl	3.51	2.17	66.7 μ
KCl	2.59	1.99	78.0 μ
KBr	2.30	2.76	94.0 μ
KI	2.44	3.07	115.0 μ
CaF ₂	4.79	2.18	53.1 μ

Madelung (18), Sutherland (19) and Einstein (20) showed independently that the natural frequency ν depends upon the three quantities, A the atomic weight, ρ the density and κ the compressibility. From dimensional considerations it follows that ν must be capable of expression by a formula of the type

$$\nu = \text{const.} \sqrt{\frac{d}{m\kappa}},$$

where d is the distance apart of the atoms and m their mass.

If now the atoms be assumed to form a cubical space lattice of side d , $\rho = \frac{m}{d^3}$, and as $m = \frac{A}{N}$, when N is Avogadro's number,

$$\nu = \text{const.} A^{-\frac{1}{3}} \rho^{-\frac{1}{6}} \kappa^{-\frac{1}{2}}.$$

If a diatomic compound be considered, A is replaced by

$$M = (M_1 M_2)^{\frac{2}{3}} / (M_1 + M_2)^{\frac{1}{3}},$$

where the M 's are the atomic weights of components. Einstein evaluated the constant above indicated by making the approximation that only the twenty-six neighbouring atoms produced effective fields of force upon any one displaced atom, and obtained a numerical value of 2.8×10^7 .

Lindemann (21) has suggested a means by which the frequency ν may be determined at the temperature of melting. If the atoms in a space lattice are vibrating, then the amplitude can never exceed the lattice spacing, and the attainment of this limiting condition

is then characteristic of the melting temperature. From the theory of equipartition of energy, the energy of an oscillator of three degrees of freedom is, at the melting temperature T_s , equal to $3kT_s$, which may be expressed in terms of the amplitude a and mass m as $3kT_s = 2\pi^2\nu^2ma^2$. Since $a = d$, $\nu = \sqrt{3kT_s/2\pi^2md^2}$. As before

$$m = \frac{A}{N} \quad \text{and} \quad \rho = \frac{m}{d^3},$$

whence

$$\nu = \text{const. } A^{-\frac{5}{6}} \rho^{\frac{1}{3}} T_s^{\frac{1}{2}}.$$

The constant is equal to 2.8×10^{12} .

Braunbek (22) has modified this formula, and replaced the constant by a function of M_1 and M_2 , the weights of the vibrating atoms, obtaining for the frequencies so derived a much greater correspondence with observation than is provided by Lindemann's formula. For details see Appendix (p. 165).

Grüneisen (23) derived a formula connecting ν with the coefficient of thermal expansion α of a substance and with the specific heat C_v at constant volume. The formula is $\nu = 2.9 \times 10^{11} \cdot A^{-\frac{2}{3}} (C_v^{\frac{1}{2}} \alpha^{-\frac{1}{2}} \rho^{\frac{1}{3}})$ and the quantities within the bracket have the values which would be expected at the absolute zero of temperature (see p. 162).

An expression found by Debye (24) for ν_{max} , the upper limit of the elastic frequency, is $\nu_{\text{max}} = \left[9N\rho/4\pi A \left(\frac{1}{c_l^3} + \frac{2}{c_t^3} \right) \right]^{\frac{1}{3}}$; c_l and c_t are the velocities of propagation of longitudinal and transverse waves. This expression may be written in terms of the elastic constants of the substance instead of the velocities of propagation; ν_{max} is then found to be equal to $5.2 \times 10^7 \cdot A^{-\frac{1}{3}} \rho^{-\frac{1}{3}} \kappa^{-\frac{1}{2}} f(\sigma)$, where σ is Poisson's ratio, and this expression is in fact only a more exact form of the Einstein-Madelung equation given above.

That the value of the characteristic vibration frequency is a quantity of fundamental importance has already been stressed, but that in the case of an element it varies with the atomic weight has been shown by Biltz (25). A sketch of his curve is given in

Fig. 18. It will be recognized that this curve is similar to the atomic volume curve originally brought forward by Lothar Meyer.

This is to be expected from the fact that theoretical methods of estimation of ν all involve both the density and the atomic weight,

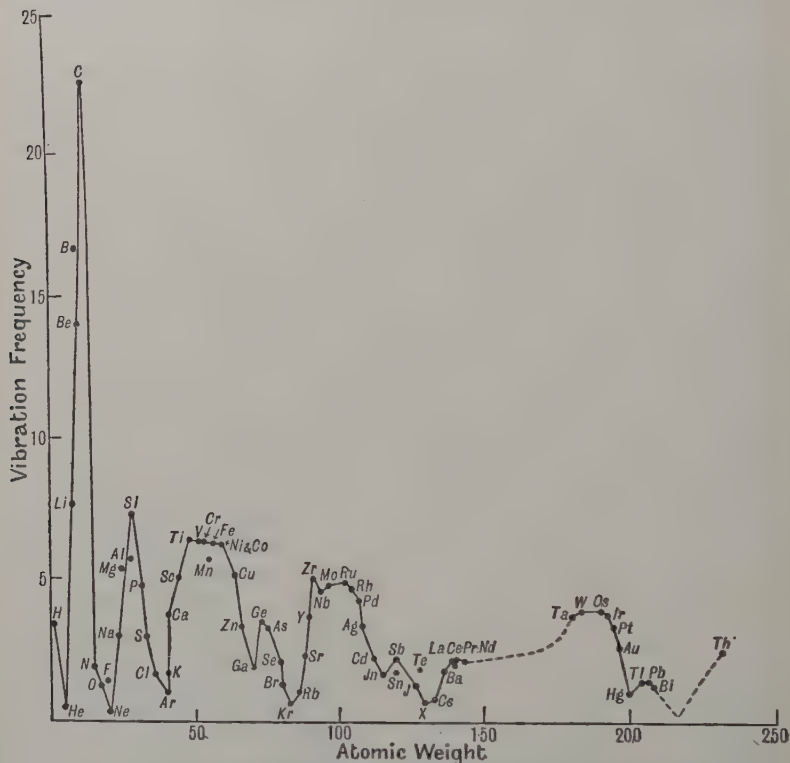


Fig. 18. The periodic variation of characteristic frequency with atomic weight (Biltz).

but that the introduction of the various quantities concerned in the formulae preserves the periodic relationship between ν and A is noteworthy.

Finally there should be mentioned an empirical rule first enunciated by Haber (4) to the effect that the infra-red characteristic

frequency and that in the ultra-violet are connected by the so-called square root formula

$$\nu_{\text{infra-red}} = \nu_{\text{ultra-violet}} \sqrt{\frac{m}{M}},$$

where m is the mass of the vibrating electron and M that of the vibrating atom. For diatomic compounds M is replaced by $\frac{1}{2}(M_1 + M_2)$. This result may be deduced by assuming a law of force varying as the first power of the displacement, and considering the atom and the electron to vibrate independently; but both these assumptions are most questionable. The rule however represents the facts, especially for liquids, to a certain degree of approximation, and this can scarcely be ascribed to chance.

As a summary of the foregoing, it may be recalled that there are eight methods of determining the characteristic frequency ν .

- (1) From the dispersion.
- (2) From Reststrahlen.
- (3) From Born's formula involving ϵ .
- (4) From Einstein's formula involving κ .
- (5) From Lindemann's or Braunbek's formula involving T_s .
- (6) From Grüneisen's formula involving α and C_v .
- (7) From Debye's formula involving the elastic constants.
- (8) Haber's square-root rule.

It will be seen that these eight methods all give frequencies of vibration which are of the same order of magnitude, and which indeed lie closely together. That the various mechanical methods of obtaining a value of the characteristic frequency of vibration ν by consideration of the elastic properties of the substance as apart from the electrical behaviour of the crystal lattice, all refer to the same vibration, and that they give slightly differing numerical values, is due to the approximate nature of the processes by which each formula is obtained, is fairly evident. That the remaining methods of optical dispersion, Reststrahlen, absorption, and Born's calculation from the dielectric constant of the material, all refer

Results from different methods of calculating the characteristic frequency.

Substance	Debye, Elastic	Debye, Thermal (Specific Heat)	Einstein, Elastic	Grüneisen, Thermal Expansion	Lindemann, from Melting Temperature	Braunbek, from Melting Temperature	Havelock, calculated from Rest- strahlen	Drude, from Dispersion	Haber, from Ultra- violet	Born, from Dielectric Constant
Pb	1.49	1.83	1.57	2.16	1.85	—	—	—	2.5	—
Cd	3.48	3.50	3.65	—	2.80	—	—	—	—	—
Ag	4.39	4.50	4.60	4.32	4.40	—	—	—	4.6	—
Cu	6.81	6.60	7.10	6.69	6.8	—	—	—	7.2	—
Al	8.26	8.30	8.65	7.68	7.8	—	—	—	8.2	—
Fe	9.67	9.45	10.1	8.49	8.3	—	—	—	—	—
NaCl	—	5.87	6.38	—	7.4	4.5	4.85	5.25	9.94	4.50
KCl	—	4.80	4.73	—	5.65	3.4	4.13	4.46	7.46	3.85
KBr	—	3.70	—	—	4.50	2.7	3.17	—	—	3.19
KI	—	—	—	—	—	2.3	2.61	—	—	2.61
CaF ₂	—	9.90	10.6	—	11.8	—	7.52	12.50	11.8	5.66

$$\nu = x \times 10^{12}.$$

to the same electromagnetic vibration associated with the movement of electric charges situated on the various atoms composing the crystalline lattice is also unquestionable. The closeness of the numerical values obtained by the mechanical and the optical methods is striking, and tempts one to believe that the two frequencies, optical and mechanical, are one and the same vibration. Indeed, it is hardly possible to picture any system in which this is not true and yet there is outstanding the great difficulty that whereas the specific heat of non-ionic materials is usually accounted for by a Debye function employing the mechanical frequency, the specific heat of polar salts where electromagnetic vibrations are possible is only to be explained by the addition of a Debye function of the elastic frequency to an Einstein function of the electromagnetic frequency. This appears to militate against any attempt to identify the mechanical and optical vibrations, and yet the hypothesis that these are two different entities is difficult to believe.

The short wave-length region, $\lambda < 30\mu$

In this portion of the spectrum, as in others, there is a possibility of the vibrations being either active or inactive. As there are no theoretical methods available for the determination of purely mechanical oscillations lying within this range of frequencies, progress is dependent entirely upon the optical methods of experiment which bring to light only those vibrations which concern alterations in electric moment.

Since work with the shorter waves can be accomplished by the use of prism spectrometers, it is natural to expect a much greater degree of resolution and dispersion than has been found possible in the far infra-red. Consequently, a more detailed knowledge of the fine structure of the bands, both in reflection and absorption spectra, has been reached.

Another factor having great influence on the refinement of measurement is the increased intensity $E, \delta\nu$ of emission of radiation from most sources for these short wave-lengths. A direct result

of this is that, working with recording instruments of the same degree of sensitivity as those used in other regions, it is feasible to reduce the slit width very greatly from that which is the minimum in work upon longer waves.

Early in the history of the subject it was recognized that the bands exhibited by many materials within a frequency range of wave-lengths 1μ to 30μ have a very different origin from those lying in the far infra-red, usually investigated by the method of Reststrahlen. Whereas these latter can be associated with mutual vibrations of the basic and acidic groups, those of higher frequency are attributed to internal oscillations within those groups themselves.

As a general rule, only compounds possessing complex radicles show bands in this region.

That the bands observed are due to vibrations within these groups is clear from the fact that, if a whole series of compounds characterized by a common radicle, either basic or acidic, be examined, it is found that certain frequencies of absorption or reflection persist throughout, being only slightly affected in the transition from one member of the series to another. Even in solution these compounds continue to exhibit their characteristic oscillations; and since in solution the radicle is a free ion, the vibrations are clearly within the radicle itself.

Infra-red investigation thus provides additional evidence for the view that the structure of a complex radicle remains the same whether it is in solution or in the crystalline state.

The natural inference is that the atoms or ions composing the complex radicle are firmly bound together, the linkage being much stronger than that existing between basic and acidic groups. The latter bond is ruptured in the process of solution and ionization, whereas the coupling within the radicle survives almost unchanged.

This strength of binding is further indicated by the comparatively high frequency of the internal oscillations.

Because the ultimate aim of infra-red spectrum analysis of solids is the determination of the structure and properties of the molecular assemblages, it is of interest to predict, on the basis of suitable models, the frequencies and intensities of the bands. These predictions can then be tested by reference to experiment.

Reasonable agreement between theoretical anticipations and experimental results will be taken as evidence that the model does indeed bear considerable resemblance to reality. As an example of such an argument, Kornfeld (26) has deduced the characteristic frequencies of vibration of the components of the CO_3 group of the carbonates.

Calculation of the frequencies characteristic of the CO_3 group

X-ray evidence, from the analysis of calcite and a number of other carbonates, points to a structure for the CO_3 group in which the oxygen centres occupy the vertices of a plane equilateral triangle, the carbon being situated at the centroid.

Kornfeld (26) has been compelled in his calculations to make the simplification of treating the CO_3 group as an isolated unit in free space. He has assumed for the purposes of his treatment that the carbon and oxygen atoms are completely ionized, i.e. C^{++++} and O^{--} giving CO_3^{--} , so that the chief binding forces are those of the electrostatic attraction between the charges. In order to stabilize the system, he postulated the existence of a repulsive field between the ions, of potential varying as the inverse fifth power of the distance.

On calculation of the potential of the CO_3 group, a further term is introduced, because of the forces between electric doublets produced in the core of each ion by deformation of its electronic shell. The electric moment \mathbf{p} of these doublets is defined by the equation $\mathbf{p} = \alpha \mathbf{E}$, where \mathbf{E} is the electric intensity and α is Born's deformability constant. α represents the electric distortion of the ion in question, when under the influence of a field of unit intensity.

The solution of the equation so constructed for the potential of

the CO_3 group leads to four characteristic vibrations, three of which involve a variation in the electric moment of the group. The fourth frequency is unaccompanied by a change in the electric moment, and therefore is incapable of direct observation, since it is without effect on the passage of electromagnetic radiation.

This fourth type of vibration is clearly due to the symmetrical expansion and contraction of the CO_3 group as a whole, for in such a mode the centre of gravity of the negative electrical charges remains at the centroid, superposed upon that of the positively charged carbon.

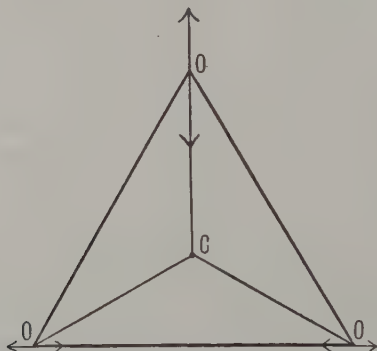


Fig. 19. One mode of vibration of the CO_3 group.

Brester (2) has analysed the vibrations on the basis of symmetry considerations, and it appears that the vibration calculated by Kornfeld to lie at a wave-length of *c.* 15μ is due to the movement of any one oxygen atom along the appropriate median, together with a small alternate elongation and diminution of the opposite side of the group, as shown in Fig. 19. The vibration at *c.* 7μ is due to the oscillation of the carbon ion in the plane of the group, either along or perpendicular to any median; the remainder of the group, to a first approximation, may be taken as rigid.

These two vibrations (*c.* 7μ and 15μ) are accompanied by change of electric moment in the plane of the CO_3 group, and consequently react with radiation having an electric vector lying in this plane.

The third active frequency (*c.* 11μ) is caused by drumhead or

membrane-like vibration of the group, the carbon ion oscillating perpendicularly to the plane of the group; in consequence this frequency is stimulated by radiation having its electric vector polarized at right angles to that which is effective in the two previous cases. Rolan (27) has published his calculations of the SO_4 frequencies at 9μ and 16μ by an analogous method.

Experimental work in the short wave-length region

A very large amount of experimental work has been done in the examination of both the absorption and reflection spectra of solids. The earlier work has however been subject to one great defect, namely, the paucity of points of observation along the spectrum. As a consequence, the curves of the earlier investigations, such as those of Coblenz (28), Nyswander (29), though of great interest in that they show the general course of the absorption or reflection, are often of little or no use to the critic who is searching for accurate determinations of wave-lengths, or coefficients of reflectivity or of absorption, as material for some generalization. It is indeed only of late that the importance of the absolute values of these coefficients is becoming apparent; investigators are urged to pay increasing attention to the accuracy of their results in this respect. In the past experimenters have frankly contented themselves with determination of wave-lengths of the maxima of absorption. They have entirely neglected to estimate the absolute values of the absorption at these points, or even if some attempt at this has been made, to allow for the corrections imposed by the finite width of the spectrometer slits.

Among those who have made accurate measurements of the infra-red spectra of solids are nevertheless to be found quite a number of workers, such as Schaefer (30), Schubert (31), Bormuth and Matossi (32), Reinkober (33), Pfund (34), Rawlins (35) and Taylor and Rideal (36), Laski (37) and Tolksdorf (38), who have endeavoured to push their measurements to considerable refinement of accuracy, at any rate in the matter of wave-length determinations.

At various times they have examined

Carbonates (31)	Selenates (41)
Nitrates (39)	Chromates (41)
Chlorates (40 and 37)	Metasilicates (42)
Bromates (40 and 37)	Ammonium compounds (33)
Iodates (40 and 37)	Oxides (38) and hydroxides (43)
Sulphates (31)	

also non-metallic substances such as carborundum (44) and sulphur (8).

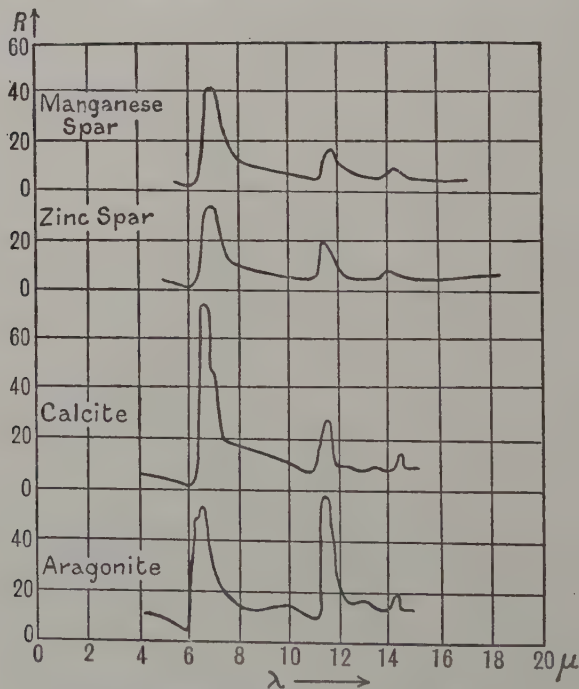


Fig. 20. Reflection spectra of various carbonates.

Of these the most immediately of interest are those with acid groups of the type BX_3 or BX_4 , where theoretical considerations of the various kinds discussed may lead to some predictions which stand or fall by the experimental results.

Generally speaking, the carbonates and nitrates fulfil expectations by giving three intense bands both by absorption or by

reflection, corresponding to the three fundamental vibrations. In the case of the carbonates(31) Schaefer finds by reflection (Fig. 20) three frequencies (c. 7μ , 11μ and 14μ), which are moreover polarized with the electric vector in directions agreeable to the theoretical deductions of Brester(2) and Kornfeld(26) and which also are in good numerical correspondence.

In his work upon the absorption spectra of these substances(32) he shows clearly the influence of the metal ion upon the exact position of the frequency characteristic of the CO_3 group (Fig. 21). This influence was necessarily omitted in Kornfeld's theoretical treatment, but more refined methods of attack might succeed in describing such a shift of frequency from one member of the series to another.

Not only the influence of the metallic ion, but also the whole environment of the CO_3 group must be taken into account, for Rawlins and Rideal(35) have shown that the characteristic frequencies differ perceptibly in the two crystalline forms of CaCO_3 , calcite (trigonal), and aragonite (rhombohedral).

The nitrates(39) show a great similarity to the carbonates, and the spectra should be capable of a similar theoretical explanation.

Further examination of the band in Calcite at 7μ

Matossi and Dane(45) measured five pieces of calcite cut parallel to the optic axis, in polarized radiation, usually having the plane of polarization perpendicular to the plane of incidence. Each crystal was examined first with the optic axis in the plane of incidence, secondly with the axis perpendicular to this plane.

By making measurements of the value of the absorption and reflection coefficients for each particular wave-length of incident radiation, it was possible to substitute these experimental values in a Drude dispersion formula and so to determine the index of refraction for both the ordinary and extraordinary rays, and to demonstrate its variation with wave-length. The index for the ordinary ray is small within the region of selective absorption and becomes a minimum at 6.6μ ; and this corresponds to the fact that

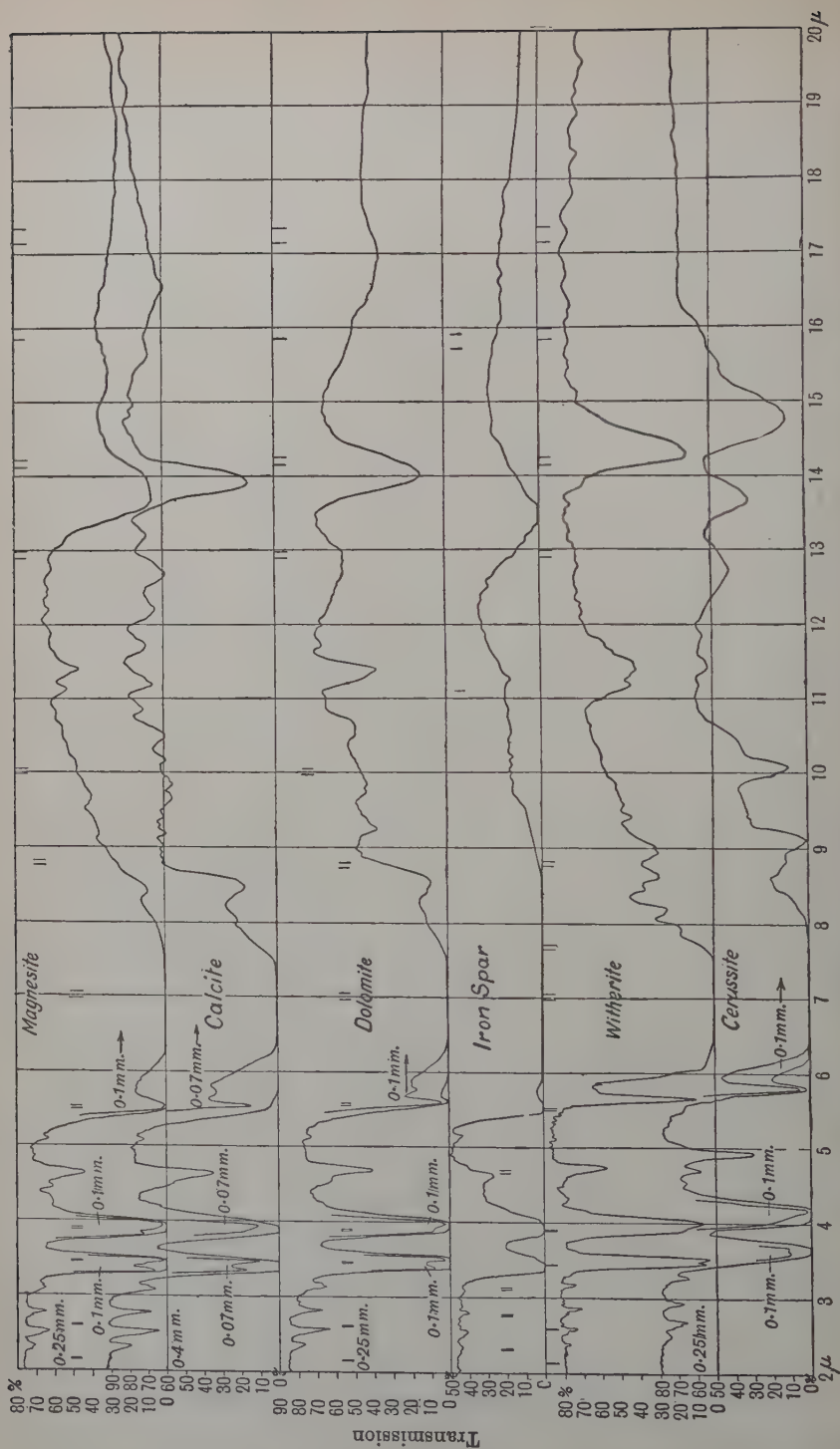


Fig. 21. The absorption spectra of various carbonates (Schaefer, Bormuth and Matossi).

the absorption is due to vibration of an electric doublet in the plane perpendicular to the optic axis. On the other hand, measurements with the extraordinary ray give a constant value of 1.5 for the refractive index, in agreement with the fact that this ray does not suffer any selective absorption.

The microscopic asymmetry of carbonates and nitrates

The reflection spectra of the carbonates and the nitrates have been the subject of a minute analysis by Schaefer, Matossi and Dane(46). They come to the conclusion that an arrest which is evident in some of the curves at 6.5μ is due to absorption by water vapour in the atmosphere and may be neglected. Calcite, when measured with an accuracy of 0.005μ , shows in its reflection spectrum two maxima at 6.685μ and 6.975μ . Other carbonates show less well-defined curves which they give as having only single maxima:

Dolomite 6.775μ , Strontianite 6.69μ ,
Aragonite 6.77μ .

However, measurements of the first overtone of these frequencies about 3.5μ all show, without exception, double maxima, and Schaefer and his colleagues argue from this that the fundamental at *c.* 7μ is also double in all cases, even when the reflective curves do not definitely show the effect. It remains to account for this doubling of the fundamental frequency and they assume a distortion of the CO_3 group in some direction in its own plane. In order that such a distortion shall not affect the symmetry which is definitely trigonal from a macroscopic standpoint (as is shown not only by the crystallographic characteristics of the material, but also by the complete symmetry of the reflecting powers of the crystal at 7μ when cut perpendicular to the optic axis, no matter what the azimuth of the plane of polarization of the incident beam), it then becomes necessary to assume the distorted CO_3 groups to be arranged with their longer medians at angles of either 30° or 60° . In this fashion may be produced a macroscopically trigonal structure, despite the lower symmetry of the CO_3 groups themselves.

Nitrates, on the other hand, show a trebling of the reflection maximum at the corresponding position of selective reflection, or a doubling in the case of uni-axial nitrates. This is only to be accounted for by a distortion of the NO_3 group in such a way that it is no longer a planar structure but is pyramidal with the nitrogen at the vertex. The fine structure of the reflection bands is then explained by assuming a suitable disposition of these pyramidal groups, parallel and perpendicular to the optic axes.

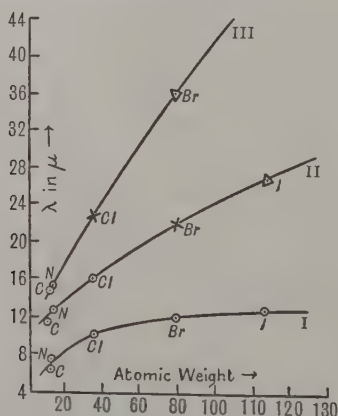


Fig. 22. Characteristic frequencies of groups of the type BX_3 .

- Experimental points due to Schaefer and Schubert.
- × Experimental points due to Laski.
- △ Extrapolated points due to Laski.

Groups of the type BX_3

In the case of the bromates, chlorates, and iodates, Schaefer(40) found only one or two fundamental frequencies, in contradistinction to the carbonates and nitrates where three fundamentals are found, in agreement with the theoretical predictions of Brester. This is only due to the limitations imposed by experimental method, and Laski(37), using a series of different Reststrahlen as sources of monochromatic radiation, pushed the analysis into regions of longer wave-length and found in the chlorates the expected number of fundamentals. In the case of the bromates and iodates it is to be

supposed that the third frequency lies even further beyond the long wave-length limit of her experiments, since the expected number does not appear.

The final results for these salts are therefore

Chlorates	10.6 μ	16.0 μ	25.0 μ
Bromates	12.2 μ	23.0 μ	36.0 μ
Iodates	12.8 μ	27.0 μ	—

Laski supposes the groups to be triangular with the halogen atom at the centroid, but does not believe the atoms to be completely ionized.

Additional bands

(i) Overtones

The absorption spectra of the carbonates⁽³²⁾ appear to be much more complex than the corresponding reflection spectra⁽³¹⁾, which only exhibit bands due to the three active fundamentals. If the law of force tending to restore a displaced atom in a lattice be anharmonic, i.e. if it varies as any even power of the distance, not only does resonance occur for the fundamental frequency ν , but also for a series approximately 2ν , 3ν , 4ν , etc. As the existence of thermal expansion in a crystal implies such an anharmonic law of force, it is not surprising that these overtones are observed in absorption spectra. They are not, as a rule, to be expected to appear in reflection measurements because of the comparative insensitivity of this method:

$$R = \frac{(n-1)^2 + n^2 K^2}{(n+1)^2 + n^2 K^2},$$

where n is the refractive index and K the absorption coefficient, so that naturally R only shows a pronounced maximum when K is very large. Small values of K_{\max} do not yield any observable local increase in R .

Schaefer and his pupils explain the bands at $c. 3.5\mu$ and $c. 2.3\mu$ in the carbonates as being the first and second overtones of the fundamental at $c. 7\mu$ (32).

It is important to notice that these and other overtones are often split into double or even triple bands, e.g. the first harmonic at $c. 3.5\mu$ appears in calcite as a doublet of separation $0.12\mu^*$.

These harmonics, if such they be, are found not to occur at wave-lengths which are exact sub-multiples of the corresponding fundamental: it has been suggested that this can be accounted for by the introduction of a correction term analogous to that used by Kratzer(47) in the explanation of the band spectra of gases. Nothing more than the crudest of approximations is claimed for this idea, but Rawlins and Rideal(35) have been able to establish that for the two modifications, calcite and aragonite, the correction is numerically greater for the less symmetrical form, aragonite.

Since both this correction and also the coefficient of thermal expansion of a crystal are functions of the anharmonic forces, it would naturally be inferred that these two quantities should increase together. This is actually found to be true, for the coefficient of thermal expansion of aragonite is some four times greater than that of the more symmetrical calcite.

(ii) *Combination tones*

A further consequence of the anharmonic nature of the forces within a crystal is the production of combination tones, i.e. the appearance of absorption bands at frequencies which are the sum or difference of integral numbers of two or more fundamental frequencies of vibration. This has been shown by Schaefer in his papers, previously mentioned, to be undoubtedly the case in the carbonate series of crystals.

Thus, for example, the two fundamentals at 7μ and 14μ combine to give a combination tone lying near 4.6μ . A large number of

* Dennison (private communication) has suggested that a repetition upon the basis of the wave mechanics of the calculation of the potential of the CO_3 group would furnish a complete explanation of the observed effects.

other bands may be similarly interpreted, although it is to be noted that in so doing Schaefer has neglected to take into account the influence of the direction in which the component vibrations take place. He also employs the inactive frequency (c. 8μ , Kornfeld(26)) as one of the components, and this seems somewhat artificial.

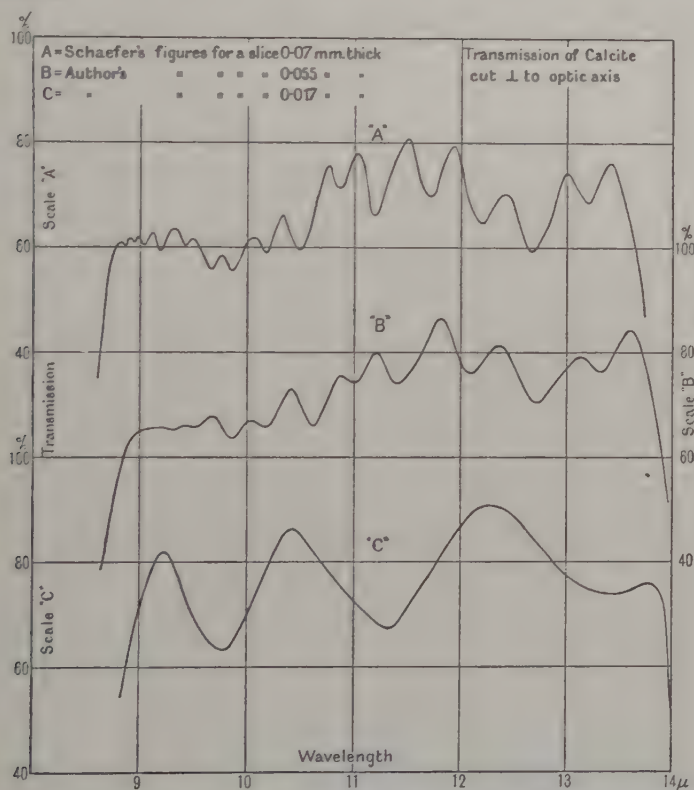


Fig. 23. Interference effects in different thicknesses of calcite. (Taylor and Rideal.)

(iii) Interference bands

Schaefer has attempted to explain a great many of the minor bands beyond $\lambda > 8\mu$ as due to combination in the way above mentioned. He uses sometimes difference tones between the short wave vibrations and more often summation tones made up

of the fundamental at 14μ together with an appropriate fundamental, lying in the long wave-length region beyond 30μ and belonging to the swinging of the CO_2 group as a whole against the metallic ions. This may indeed be so, but in calcite most of the bands between 8μ and 14μ have been shown by Taylor and Rideal (36) to be caused simply by interference effects within the crystal slice. See Fig. 23.

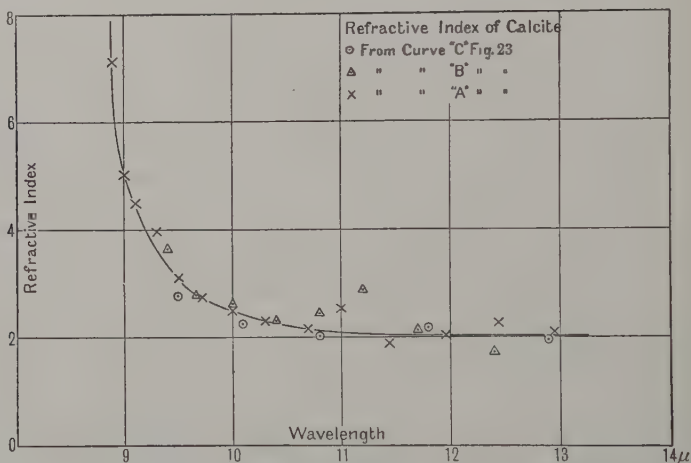


Fig. 24. The refractive index of calcite calculated from the interference bands of Fig. 23. (Taylor and Rideal.)

They have moreover calculated the refractive index of calcite between 8μ and 14μ from observations upon several crystals of different thicknesses, and have succeeded in showing that the refractive index curve possesses the usual shape expected from the Drude theory, attaining the high value $n = 7$ immediately on the long wave-length side of the absorption band at $c. 7\mu$.

A further paper by Taylor(48) continues this analysis of the spectral band. He uses the partial polarization produced in radiation transmitted through a calcite slice when the wave-length approximates to that at which true absorption is present, as distinct from that at which there is an apparent decrease in intensity of transmission owing to interference within the slice. By this means,

using two crystals cut parallel to the optic axis, and rotating one about the transmitted ray, he finds a relative measure of the amount of polarization produced by taking the ratio of the intensity of transmission when the axes of the two crystals are parallel to the intensity when the axes are perpendicular. This ratio increases when absorption increases, and so if this be plotted against the wavelength of the incident radiation, a curve is obtained showing by its

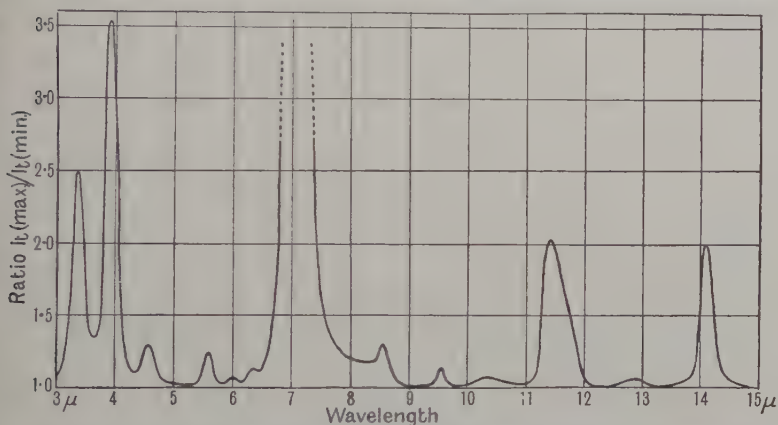


Fig. 25. Curve showing maxima of polarization and therefore of absorption coefficient for calcite. (Taylor.)

maxima the regions of greatest absorption (Fig. 25). Taylor not only differentiates in such a fashion between true absorption bands and the spurious effects of interference, but he endeavours to show that the spectrum when thus simplified can be explained by means of combination tones, without following Schaefer in assuming the influence of the "inactive vibration" in such combinations.

The explanation of spectra

The explanation offered by Schaefer that the multiplicity of absorption bands in the spectra of the carbonates is due to combination tones set up between the various fundamentals is more fully accepted by Joos(49). He supposes a formal analogy to exist between gaseous and crystalline spectra. Corresponding to pure rotation in

the long wave-length region, and intramolecular vibration in the short waves in the spectra of gases, there is to be found in solids two regions, one of absorption of long waves, due to vibrations of the lattice structure (i.e. Reststrahlen), and one of absorption of short waves due to interatomic vibrations within complex groups. In both cases of gaseous and crystalline spectra there are, in addition, regions of absorption which may be traced to electronic mechanism usually in the short wave visible or ultra-violet. As for gaseous spectra, so for crystalline spectra, in general any or all of these vibrations may be compounded to give secondary regions of absorption. Thus, as in the familiar fine structure of gaseous spectra, due to superposition of rotation terms upon the vibration terms, so in crystalline spectra a series of bands may be noticed which have constant frequency difference equal to some frequency of absorption in the far infra-red.

To observe this effect Joos found it necessary to use compounds of which the anion possessed powers of absorption at different wave-lengths from those at which the cation was effective. Particular attention must be paid to the fact that the region of absorption of the crystalline unit is not necessarily the same as that of the same unit in the free ionic state.

There is a further peculiarity in that, since the forces of cohesion in the crystal are never harmonic, more quantum switches can occur than are given by the correspondence principle, and hence the spectra are often more complex than would be expected.

As an example of Joos' work may be noticed the visible spectrum of the alums, e.g. $\text{K}_2\text{SO}_4\text{Cr}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$, in which eleven terms occur with a constant spectral difference of wave-number equal to 43 cms.^{-1} . If this is to be explained on the above lines, there is indicated a frequency of vibration which should give rise to Reststrahlen from the crystal, of wave-length $\frac{1}{43} \text{ cm.} = 232\mu$. There are also noticeable doublets of interval of 300 wave-numbers each, indicating that the group $\text{Cr}(\text{H}_2\text{O})_{12}^{+++}$ should possess characteristic oscillations of wave-length about 33μ .

The only remaining instance wherein theoretical anticipations may be compared with experiment is that of the sulphates. In their reflection spectra Schaefer and Schubert(31) show that they possess only two characteristic frequencies at approximately 9μ and 16μ (Fig. 26). Rolan's(27) investigation agrees reasonably well with this.

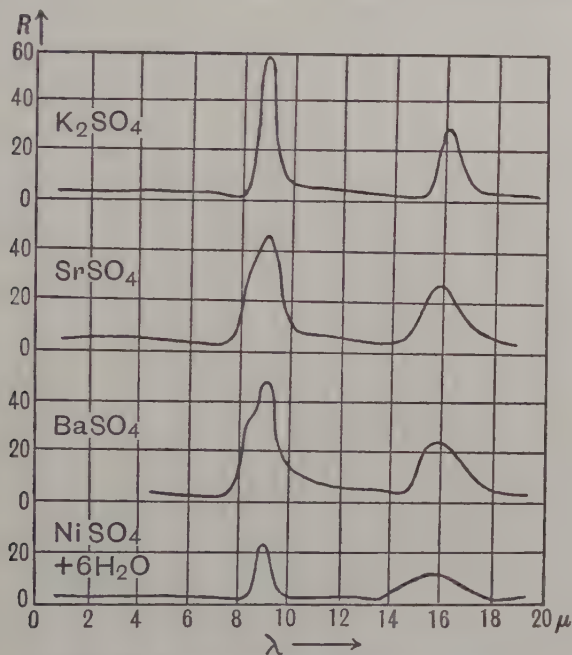


Fig. 26. Reflection spectra of some sulphates.

A spectrum very similar to that of the sulphates is provided by the ammonium salts, which were examined by Reinkober(33). The NH_4 group here may be considered to be what Goldschmidt would call the anti-type of the SO_4 group; i.e. it is tetrahedral with the nitrogen at the centroid, exactly similar to the SO_4 group, save that the changes are different and the signs are reversed. Hence it is that the NH_4^+ and SO_4^{--} groups give such similar spectra—the smaller charges on the former group being compensated for by the smaller mass of the component atoms.

In recent work Tolksdorf(38) has examined several oxides in order to show that the infra-red spectra are dependent upon atomic environment. She chose MgO and CaO, two oxides of which the Goldschmidt co-ordination number is 6, i.e. crystals of the rock-salt type, and BeO and ZnO, two of which the co-ordination number is 4, i.e. crystals of the wurtzite type. The experimental technique provides some features of especial interest, as these sub-

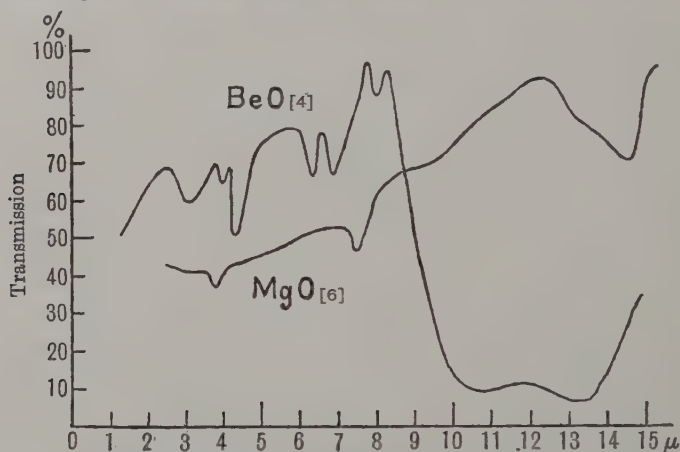


Fig. 27. Absorption spectra of crystals of different co-ordination numbers.

stances could only be obtained in powder form; it will be referred to in the following chapter. The results, however, quite definitely show greater complexity of spectra for the less symmetrical arrangements—i.e. BeO and ZnO. Fig. 27 compares the spectra of BeO and MgO. The considerable intensity of absorption in several instances might appear to argue an ionic structure.

Ionization of atoms

It may be as well to notice here the bearing of the ionic or non-ionic nature of the groups upon the type of infra-red spectra obtained. In the case of polar salts where the units are unquestionably ionic, such as NaCl, KBr, etc., the forces are so related to the masses that the vibration is a slow one lying far out in the infra-red spectrum. In the case of groups like CO_3 , NO_3 , SO_4 , etc., where the charges

borne by the central atom can be quite large, the infra-red spectrum always shows the presence of comparatively rapid vibrations, usually corresponding to wave-lengths from 6μ to 15μ or 20μ . This undoubtedly indicates that even though the central atom may exert very great polarizing power upon the external atoms of the group, thereby largely modifying the forces of cohesion and consequently the periods of characteristic vibration, yet the atoms are fully ionized and act upon one another with the ordinary coulomb forces, which are sufficiently strong to account for the rapidity of the fundamental or characteristic oscillation.

Thus the type of infra-red spectrum may be made a valuable criterion of the nature of the forces within the complex radicles, and consequently of the state of ionization of the component parts. Such an argument may even be extended to a non-metallic compound such as silicon carbide(44), where intense reflection bands are found in the short infra-red region, which may thus be taken as indicative of the ionic nature of the units Si and C, one having a negative charge the other a positive charge, in spite of the family resemblance between the two atoms. In the following paragraph evidence is mentioned for supposing a similar behaviour even among the atoms of the element sulphur.

Active vibrations in non-metals

In all the work described in the preceding sections, there is available a large amount of X-ray data concerning the crystals in question, but such data in connection with non-metallic elements is meagre.

From what has already been said, absorption bands in the spectrum can only occur when there is present in the elementary group of the substance some electric moment which is capable of variation in response to an impressed field. Non-metals in the elementary state are not usually thought to possess such electric moments, but it has been pointed out(50) that increase in Born's constant α is accompanied by increase in compressibility. In general,

the non-metals possess high compressibility, and therefore a high value of α , which may be supposed to facilitate the production of an electric moment within the elementary group.

In the case of a typical non-metal, sulphur, Taylor and Rideal⁽⁸⁾ have proved that not only do absorption bands of considerable depth occur in the infra-red spectrum, but that they persist

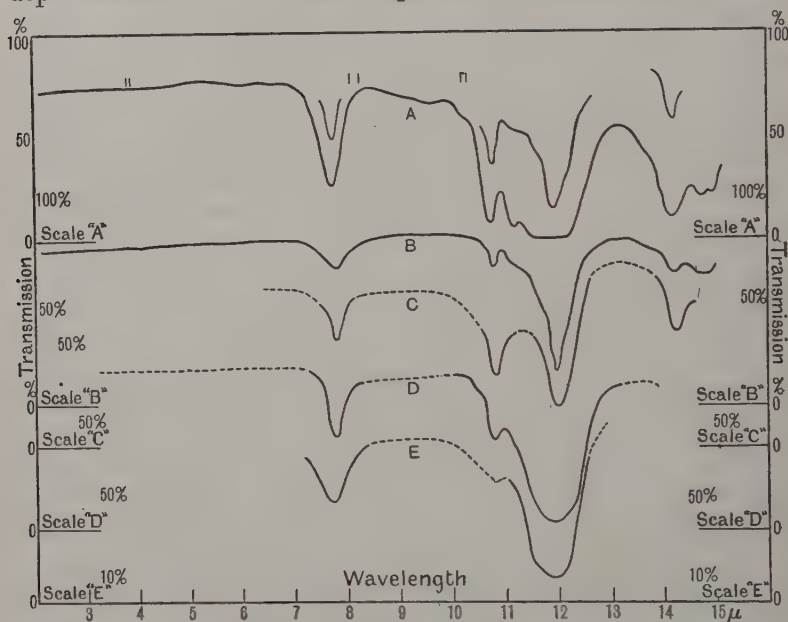


Fig. 28. The absorption spectrum of sulphur. (Taylor and Rideal.)

Curve *A*. Rhombic sulphur at 18° C.; Curve *B*. Prismatic sulphur at 96° C.;
Curve *C*. Rhombic sulphur at 96° C.; Curve *D*. Liquid sulphur at 125° C.;
Curve *E*. Plastic sulphur at 18° C.

throughout the range of temperature 18° C. to 125° C. in the various solid phases, rhombic, prismatic and plastic, and also in the liquid state.

From measurement of the width and depth of the absorption bands they have deduced a value for the electric moment of the elementary group, and have shown that it agrees well with values calculated from thermal data of the heats of vaporization and

dissociation of the group S_2 . They have been able to suggest a possible structure of the unit crystal group as a result of their observations in the infra-red. This leads to the belief that sulphur atoms, even if linked homopolarly, show quite definitely alternate positive and negative polarities.

Temperature variation of vibration frequency

An interesting point in connection with these characteristic frequencies of complex radicles was noticed by Reinkober(51) in a systematic study of the reflection spectra of the ammonium salts. He established that the frequency of vibration increased with falling temperature. For example, in the NH_4 band near 7μ , a lowering of temperature from $35^\circ C.$ to $-175^\circ C.$ produced a shift of 0.02μ towards shorter wave-lengths. It also appeared that an increase of reflective power R_{max} occurs, the intensity of reflection of NH_4Cl at 7μ being more than twice as great at $-175^\circ C.$ as at $35^\circ C.$ Apparently disturbing factors which hinder the response of the group to the incident wave, even at resonance, die out as the temperature is lowered. The reason for this has never been investigated.

Taylor and Rideal(8), in the absorption spectrum of sulphur, noticed that rise of temperature shifted the position of maximum absorption towards longer wave-lengths. The shift was small, and appeared to be unaltered by the transition of the rhombic sulphur into the monoclinic form.

Reinkober(52) has recently examined the change of absorption coefficients with temperature for fluorite and quartz in the short infra-red region. Quartz has a region of strong absorption between 3μ and 6.5μ and fluorite between 8μ and 12.5μ . Unlike the reflection coefficient, which increases in the case of ammonium chloride with lowering of temperature, the absorption coefficients of quartz and fluorite decrease with decreasing temperature in such a manner that, if extrapolated, there is a residual absorption even at zero

temperature. The behaviour of the absorption coefficient with temperature differs in the two substances in that for fluorite the change of absorption with temperature varies linearly with the wave-length, whereas for quartz it is a maximum when the absorption is a maximum.

CONCLUSION

It is hoped that this chapter will serve as some proof that in the near future the study of infra-red spectra may become a widely used method of analysis of crystalline and molecular structure. Already it has been a valuable source of information upon the type of binding force existing between atom and atom.

While X-rays may be used as a probe to discover the static configuration of the crystal or molecule, infra-red radiation may be used to set the component parts into vibration, and to determine, from consideration of the motion produced, their dynamic behaviour.

It may be worth while to emphasize the point that in future not only will great attention have to be paid to accurate determination of the frequency at which maximum absorption occurs, but also careful measurements must be made of the intensity of absorption at each point. This is as much the case in the examination of solids in the infra-red as it was found to be in the analysis of gases.

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Chapter 4: EXPERIMENTAL

Introductory

IN this chapter will be discussed the experimental problems met with in infra-red research.

Stripped of all its elaborations, an apparatus for use in this branch of spectroscopy will consist of three essential parts:

- (a) A constant source of infra-red radiation.
- (b) A system for dispersion into a spectrum.
- (c) A means of detecting and measuring the energy density.

A treatment under these three headings will give a fair idea of procedure in the examination of absorption and reflection spectra as well as Reststrahlen or residual rays. In addition, a number of finer points, perhaps of value in particular circumstances, will be noticed. Whether the final application of the work be physical or chemical, observation generally entails the use of some form of spectroscopic arrangement, and it is for this reason that the above classification of the experimental details has been adopted, as being the one most likely to correspond to actual practice.

Sources of radiation

The source of infra-red radiation in most common use is some form of electrically-heated emitter, such as a Nernst glower, a silica pencil or similar commercial product, or in some cases a "Hohlraum," i.e. a small hollow furnace maintained electrically at a constant temperature, the radiation issuing from an aperture in one side.

The gas-heated Welsbach mantle, which was exclusively used in earlier investigations, needs no consideration now, as its emission is comparatively feeble and lacking in constancy; it has seldom found a place in research work to any marked extent for some years.

A substitute sometimes used for the silica pencil is the pre-heater supplied occasionally with Nernst glowers. It consists of a small hollow porcelain tube, closely wound with a spiral of fine platinum wire, the whole being coated with another thin layer of clayey material. A current of about 1 ampere through the winding usually suffices to keep the contrivance at a bright cherry-red heat, above which temperature it is inadvisable to work.

When using a Nernst glower as a source it is essential that the current through it be maintained at a steady value, otherwise very irregular emission will result. It is desirable to employ a battery of cells giving a fairly constant voltage, and not to attempt to run off the usual power mains. In any case, an ammeter and adjustable rheostat in series with the glower are necessary.

Most Nernst glowers on the market consume 1 ampere, but the use of a lower current (generally 0.7 ampere) lengthens their life considerably without seriously reducing their efficiency. A danger to be guarded against is their tendency to bend, for if the image of a glower is accurately focussed upon the entrance slit of the spectrometer a gradual warping of the filament during the progress of a series of observations will cause deviations from trustworthy readings.

The general stability and robust nature of preparations of silica in the form of rods* is a decided advantage in their favour. Unlike Nernst glowers they require no pre-heating. At the same time the temperature is much lower, with the result that the intensity of emission is decidedly less than that of a Nernst filament. On the other hand, the area of the emitting surface is greater, a fact which may prove advantageous when working with large slit openings; the whole area of the aperture may thus be utilized.

Glagolewa-Arkadiewa(1) has shown that it is possible to produce radiation of wave-length as short as 82μ by electromagnetic methods.

* A commercial product, "Globar," originally intended for use in domestic heating, has been successfully used by the authors. The current consumption is high, perhaps as much as 10 amperes: apparently the material may be used without detriment to itself at a temperature considerably in excess of that recommended by the makers.

For this purpose, instead of a single Hertzian oscillator which would rapidly burn out, she uses a number of oscillators, stimulated by the same discharge, consisting of fine metallic particles suspended in oil. The pasty material so formed is carried round between the points of discharge by a small rotating wheel. The wave-length increases with the size of the particles, but the energy, even in the shorter regions of wave-lengths, is stated to be quite considerable.

The Dispersive System

The dispersive system in infra-red work is much like the usual spectrometric arrangement in the visible region. On the other hand a system of mirrors must replace the collimator and telescopic lenses, because of the rapid variation of refractive index with wave-length for all materials transparent to this part of the spectrum, and the impossibility of rendering such lenses "achromatic." Speculum metal, rustless steel, silver or gold-coated glass are all effective as mirrors.

Inherent defects in the use of mirrors are the presence of spherical aberration and astigmatism, but an advantage is that the focal length is independent of the frequency of the incident radiation. Astigmatism is minimized as far as possible by designing the apparatus in such a way that the inclination of the incident beam to the axes of the mirrors is always small*.

A table giving approximate constants proportional to numerical and angular aperture of the mirrors in use with various forms of spectrometers appears on page 115. A diagram showing the general arrangement of a prism instrument is shown in Fig. 29.

Since the spectrometer is to be used for a continuous series of wave-lengths within some particular region, it must have, in addition to its optical equipment, a suitable mechanical contrivance by which the dispersive system (i.e. prism or grating) can be given any required angular orientation. It will be convenient to treat the

* Laski has discussed this and other experimental problems in the *Handbuch der Physik*, 19. 802. 1928.

spectrometer in turn under each of these two headings:

- (i) mechanical,
- (ii) optical.

Each system is subject to imperfections of its own.

A spectrometer may be expected to suffer from inherent weakness in the mechanical contrivance whereby the prism or grating table is rotated and its position recorded.

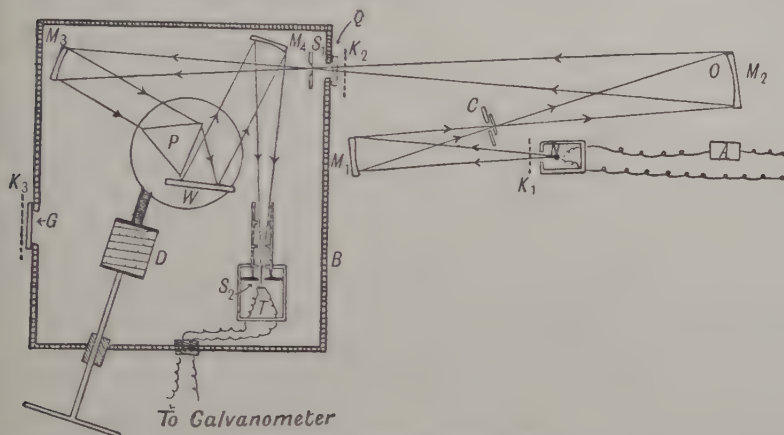


Fig. 29. A prism spectrometer.

N, Nernst glower; *M*₁, *M*₂, *M*₃, *M*₄, Mirrors; *W*, Wadsworth mirror; *P*, Prism; *S*₁, *S*₂, Slits; *T*, Thermopile; *B*, Cast iron case; *Q*, *G*, Windows; *C*, Crystal holder; *K*₁, *K*₂, *K*₃, Shutters; *D*, Wave drum; *A*, Ammeter.

A wave-length drum mounted upon a screw is a common device. The screw is arranged to bear upon a lever which projects radially from the turntable. The drum is graduated either in a system of arbitrary units, or, less advantageously, to read wave-lengths directly. It will become clear that any method of calibration entails such a large number of corrections that it is unlikely that the wave-length scale will correspond sufficiently accurately with reality for refined observations.

It is almost impossible to exaggerate the importance of cutting the thread of the above-mentioned screw with precision, and no less attention should be paid to the cutting and hardening of the

screw point which, bearing as it does upon the lever at varying angles of contact, should be perfectly symmetrical about its axis of rotation. Actually, these ideal conditions are never fulfilled, and the rotation of the table shows errors which are periodic with the revolution of the wave-length drum.

The authors can claim some first-hand experience which leads them to a genuine distrust of such systems for accurate work. It might almost be preferable to abandon completely the screw and lever method of rotation of the spectrometer table, and to rely upon a graduated circle such as is used in goniometry and surveying. Instrument technique of this kind has reached a degree of perfection unapproached by indirect methods of setting, which probably owe their present popularity more to attempts to bring spectroscopy within the bounds of laboratory routine than to the attainment of the greatest accuracy.

The validity of wave-length measurements is a complex matter, depending upon a number of factors, but unless this mechanical weakness is either allowed for by suitable corrections, or eliminated at its source by a method of the kind suggested, it is hard to credit some of the refinements which have been claimed.

An arrangement for setting the turntable by a form of worm-wheel and pinion has been introduced by Dr Carl Leiss⁽²⁾ at Professor Schaefer's suggestion. Probably it is an improvement over the screw and lever system*, but its capability of precision is unconvincing compared with that of a divided circle.

Optical Equipment

As in instruments for use in the visible region, this is of a two-fold nature, an arrangement of mirrors and slits corresponding to the collimator and telescope, and a dispersive system. Since the

* In either case, it is necessary to set the drum always in the positive direction of rotation of the screw, since no spectrometer, as far as the authors are aware, is free from backlash.

chief difficulty met with in infra-red work is occasioned by the low intensity of the radiation, it is always desirable to arrange for the use of mirrors of the largest angular aperture compatible with general convenience.

As usual, the resolving power is proportional to the numerical aperture of the mirrors, i.e. to $\frac{D}{f}$, where D is the diameter of aperture

Infra-red Spectrometers

Maker and Type	$D/f \propto$ numerical aperture	$D^2/f^2 \propto$ solid angle of entrant cone of radiation
Bellingham and Stanley. "Universal"	0.13	0.0166
Hilger. Small Model	0.14	0.0198
Large Model	0.22	0.0472
Schmidt and Haensch. Rubens	0.14	0.0193
Leiss. Small Model, 1 prism	0.21	0.0452
Large Model, 2 prisms	0.17	0.0294
Grating spectrometer	0.33	0.1110
Sleator and Imes. Prism and grating in tandem	0.20	0.0400

and f the focal length. Again, the quantity of radiation received depends upon the solid angle of the entrant cone, i.e. proportional to $\left(\frac{D}{f}\right)^2$. The values of these quantities for a number of well-known types of instruments are given above.

For the dispersive system proper, prisms or gratings are available. For prisms the materials suitable for infra-red work and the

wave-length limits, for which in practice they are useful, are

Between	1.0 μ and 4.0 μ .	Quartz.
„	4.0 μ and 9.5 μ .	Fluorite.
„	9.5 μ and 14.5 μ .	Rock-salt.
„	14.5 μ and 23.0 μ .	Sylvine.

The index of refraction of these substances as a function of the wave-length (i.e. the dispersion) has been determined by a number of investigators(3). From the dispersion it is possible to proceed with the work of calibration, in the way to be described.

It must be remembered that quartz, fluorite, rock-salt and sylvine, all possess a temperature coefficient of refractive index(4). This coefficient, although quite small in some regions of the spectrum, may become important at certain wave-lengths. It is needless to give further details of the optical constants of these materials, for a complete discussion of them will be found in Glazebrook's *Dictionary of Applied Physics* (3). The characteristic absorption bands of quartz should be noticed, as they make their presence felt very markedly in experimental work.

Calibration

In order to use a prism spectrometer for quantitative work the first essential is to establish a relationship between the radiation transmitted through the system and the setting of the prism table as recorded by the drum or vernier. In the case of instruments provided with the former it is necessary in addition to take great care to eliminate the effect of errors in the cutting of the screw thread or in the guiding of the bearing surfaces of the contact point and lever. An accurately graduated circle and vernier system should be free from appreciable error and therefore needs no further consideration.

Paschen's empirical results for the refractive indices of the materials in question, together with the usual formula for refraction through a prism at minimum deviation, may be used to lead

to the connection required between the wave-length and the drum setting: provided, either that the geometry of the system permits of a calculation being made of the deviation ϕ at every position of the drum, or, alternatively, that this deviation may be determined experimentally by goniometric methods.

The conventional procedure is to calculate the deviation for each wave-length λ given in Paschen's tables, and to plot ϕ against λ on an extended scale. ϕ may be translated into drum readings, and thus a series of some twenty points is obtained from which to plot the final calibration curve. If at this stage of the proceedings a curve be drawn through the points, the effect is to smooth out the irregularities due to errors in the mechanical system.

A scheme devised by the authors, which has the advantage first of revealing and subsequently of eliminating these vagaries produced by the screw, consists in reversing the process just described. By means of a telescope and divided circle reading accurately to five seconds of arc, a table is first of all compiled giving the deviation ϕ of a ray passing through the instrument at conveniently close intervals (about twenty per revolution of the drum).

By the use of seven-figure logarithms, and by working according to the scheme on p. 118, the refractive index n of the material of the prism corresponding to the ray passing through the instrument at each drum-setting is obtained. Then, on a suitably large scale, Paschen's figures for n are plotted against the wave-length λ , and from this curve, the column (8) of the table may be filled in. The final calibration curve is plotted from columns 1 and 8, and this curve will usually exhibit periodic irregularities at every revolution of the drum. The errors being now patent, and no longer masked by an adventitious process of smoothing out, they are once and for all eliminated.

It will be obvious that the performance of this process is of a laborious character, and may be productive of arithmetical mistakes which would result in evils far greater than those which it is the intention to combat. Experience has shown that a table such as

Specimen Calibration Table

$$A = 59^{\circ} 50' 30''. \quad \log \sin \frac{A}{2} = \bar{9}.6988058.$$

Drum	Deviation ϕ	$\phi + A$	$\frac{\phi + A}{2}$	$\log \sin \frac{\phi + A}{2}$	$\log n$	n	λ in μ
...
44.5	36° 12' 4"	96° 10' 34"	48° 5' 17"	9.8716736	0.1728678	1.48891	10.853
45.0	36° 8' 44"	96° 7' 14"	48° 3' 37"	.8714844	0.1726786	1.48826	10.943
45.5	36° 5' 14"	96° 3' 44"	48° 1' 52"	.8712857	0.1724799	1.48758	11.036
46.0	36° 1' 39"	96° 0' 9"	48° 0' 5"	.8710830	0.1722772	1.48688	11.130
46.5	35° 58' 14"	95° 56' 44"	47° 58' 22"	.8708875	0.1720817	1.48622	11.220
...

that indicated on page 118 should be built up by the completion of one whole column at a time, working only in alternate rows, and by concentrating attention upon the difference between each entry and the succeeding one, numerical blunders may be avoided with a fair degree of confidence. In this way, should an error creep in unobserved to any one odd row, it must inevitably be detected upon returning to calculate the even rows.

The foregoing treatment is directly applicable to spectrometers in which, because of the presence of a Wadsworth mirror, the prism is used at the position of minimum deviation. This is the state of affairs generally realized.

If however the Littrow principle is to be employed, in which the prism is traversed twice by the radiation, which is reflected at the back surface, then although the general method just outlined may be used, yet strictly speaking a correction must be introduced to allow for the fact that a Littrow prism is not accurately at minimum deviation. In some forms the radiation falls before and after its passage through the prism upon different mirrors, and thus the departure from the position of minimum deviation becomes considerable, and the correction becomes of vital importance.

In this case the effective dispersion is increased. Let ABC be the prism of which the refracting angle is B , usually about 30° in practice (see Fig. 30).

M_1 , M_2 are the poles of the concave mirrors of the spectrometer. By means of instrument gauges the angle M_1OM_2 is determined (an accuracy to the nearest minute will suffice), a set of trial readings is then taken, and the path of radiation followed through the system so that for the appropriate index of refraction the angle M_1OM_2 remains constant.

Thus, referring to the figure, say for a quartz prism, angle B is known from measurement, AB is reflecting back surface of the prism, OO' is bisector of "mirror angle" M_1OM_2 ;

$$\frac{\sin i}{\sin r} = n,$$

or (see figure)

$$\sin d = n \sin a,$$

$$\sin c = n \sin b.$$

Also $M_1OM_2 = d - c$ (a known constant) from which d is found. This gives the angle between the normal NN' and the emergent beam, and this angle is the quantity required.

The increase in dispersion at the three typical wave-lengths is

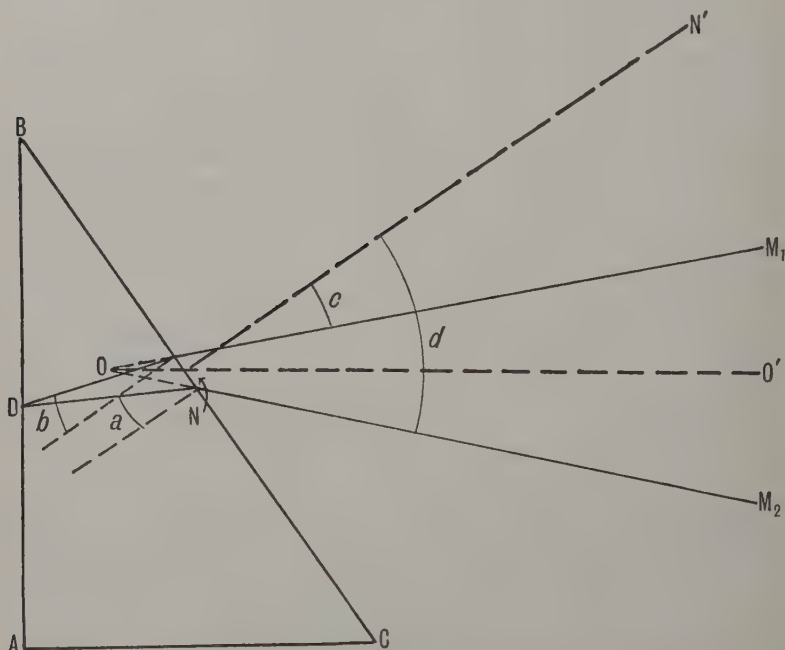


Fig. 30. A prism used at an angle different from that of minimum deviation.

now known, and permits the drawing of a curve showing the increase of dispersion against wave-length. From this curve the appropriate corrections are made to the usual calibration curve which has been constructed by assuming minimum deviation. This correction may well amount to a couple of minutes of arc (it increases with the wave-length) within the most useful portion of quartz transmission: it will be found to make a considerable difference in the second

decimal place in units of μ in wave-length settings. It is not a difference in the angle of the prism, unless it exceeds some twenty seconds or so, to which the results are so sensitive, but more to the angle subtended by the poles of the mirrors at the centre of rotation, i.e. the angle $d - c$ in the above discussion.

This angle in the arrangement due to Littrow as used by Sleator and Imes(5) is so small that the correction may be neglected when working with such an instrument.

It must not be overlooked that calibrations such as have been described depend upon a zero setting of the spectrometer drum, usually by means of the sodium lines, and this introduces difficulties on its own account. The image of a line in the focal plane of the exit slit of a prism instrument is curved. A marked difference of datum line will be obtained depending upon whether the centre of the arc or the top and bottom are, or are not, in the field of view of a narrow slit. Naturally, it is hardly profitable to attempt to estimate this ambiguity in the general case, but experience shows that it is quite noticeable.

An obvious way of escape would be to allow the image to fall upon the receiving instrument (thermopile or radiomicrometer) and to take the maximum of the corresponding deflection: this is not usually possible in practice, for the slit-width in order to obtain any trustworthy deflection would have to be so large as to render void the purpose in view*. It is not denied that this is a real practical drawback, and one for which it is difficult to see a thoroughly satisfactory remedy. One palliative is to compare, in any given region of the spectrum, the results for well-known absorption bands in crystals with those given by the apparatus under test, and to adjust matters accordingly.

It will be convenient to include within this review of the spectrometer system a brief survey of the other devices connected with the optical path of the radiation outside the instrument itself.

* It must be remembered that the energy of the radiation from a sodium flame is small.

Concave mirrors, silvered on the front surface, or rustless steel reflectors, are usually the means of bringing to a focus the rays given off from the glower. The mirrors should be mounted in holders which can be adjusted about horizontal and vertical axes, preferably by means of three screws. It must be remembered that the solid angle of the cone of radiation entering the slit of the spectrometer must be at least as great as the solid angular aperture of the instrument itself (see p. 115), and mirrors of suitable curvature and dimensions must be chosen with this end in view.

So far as the investigation of crystals is concerned it is only necessary to focus the image of the source upon the specimen under examination, and to pick up the transmitted beam and focus that again upon the entrance slit of the spectrometer. The latter instrument itself is generally arranged to give a focal image in the plane of the exit slit, and all reflecting surfaces within the spectrometer should be carefully adjusted with the help of a sodium flame to satisfy these conditions.

The radiation emerging from the exit slit should then fall immediately upon the receiving surface of the thermopile, when this is used. Where a radiomicrometer is employed, another concave mirror will be called into play to focus this monochromatic beam upon the receiving plate. It is at once evident that this latter system, while offering some decided advantages, imposes great restraint upon the configuration of the apparatus in the space available; for the whole is, in a geometrical sense, a rigid figure, and accurate orientation of each part is needed with respect to all the others.

The length of the optical path may be very considerable, amounting to nearly ten feet in one typical arrangement (see Fig. 31). It is advantageous, when setting up a spectrometer and radiomicrometer in conjunction, to concentrate attention upon the latter, settling its orientation once and for all; when this is done, the arrangement of the remaining parts of the system is comparatively simple.

The disposition of a thermopile-galvanometer system is simpler,

for the latter instrument can be in any position with respect to the rest of the apparatus. This advantage is gained at the price of having two instruments occupied in recording instead of one. Questions of relative sensitivity will be considered later on, as well as a number of other facts which influence the final choice.

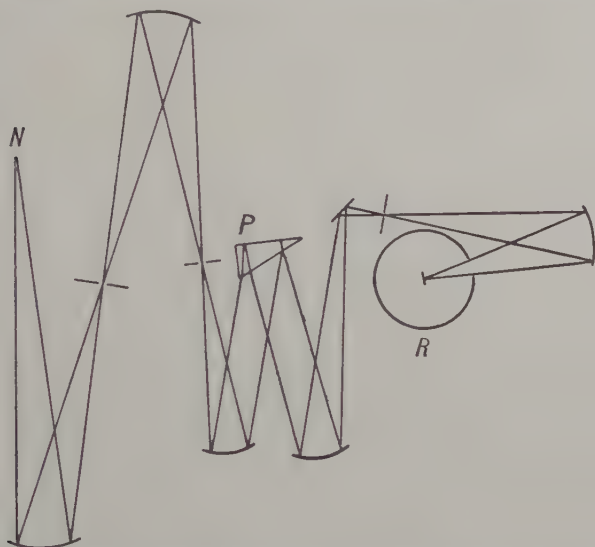


Fig. 31. An example of the optical path in an apparatus employing a radio-micrometer or radiometer *R*. *N*=source of radiation, *P*=prism.

In observations upon the absorption spectra of gases, the optical path is apt to become involved. The desirability of having a parallel beam through the absorption tubes brings this about. It is true that in some experiments mirrors of long focal length have been used, so that a narrow cone is substituted in place of the parallel beam, but in any case it is important that the radiation should pass symmetrically along the tube.

Efficient shielding of the spectrometer and its accessories from stray radiation is a vital point. A number of asbestos* screens will be required for this, and in addition double-walled casings packed

* A commercial product known as "Celotex" has been found efficient for use as shields. Galvanized iron sheeting has some advantages.

with slag-wool or cotton-wool will often help to screen a radio-micrometer or thermopile, and to equalize the temperature throughout.

Moreover the polish of the reflecting surfaces must be satisfactorily maintained; otherwise it is found that a general blunting of the absorption or reflection peaks occurs, and also that it becomes necessary to use a slit of undue width as a result of loss of energy due to scattering.

Gratings

A more fundamental method of analysing and measuring the radiation is afforded by the use of a diffraction grating, of which the main advantages are that determination of wave-length depends solely upon the accurate measurement of the diffraction angle, since the thermal coefficient of expansion of the material of the grating is the only variable factor. Calibration thus consists merely in finding the grating constant by a travelling microscope or some similar arrangement, and the angle between the incident and diffracted beams.

Gratings for use in the infra-red are of two kinds, reflection and transmission, and are almost invariably plane. Reflection gratings ruled on speculum metal, brass, or gold, or metal on glass have been used by various workers(6); transmission gratings must be of wire, owing to the general opacity of solids in the infra-red(7).

It should be remembered that a grating can only efficiently deal with a range of frequencies less than one octave, whereas the infra-red extends over some ten octaves in all. This introduces additional complexity beyond that met with in the visible region. In the case of Reststrahlen the radiation is reduced to a comparatively narrow band of frequencies, and it is possible to use gratings without more ado.

When radiation of continuously varying wave-length is to be examined, some means of avoiding overlapping of the spectrum is the first essential. In regions of wave-length for which a convenient transparent material is available for the construction of a prism

an excellent plan is to use a refraction and a diffraction spectrometer arranged in tandem, the prism of the former serving only to select a small portion of the spectrum for final analysis by the grating. Since all that is needed is to present to the diffraction instrument a narrow band of frequencies, low dispersion will suffice

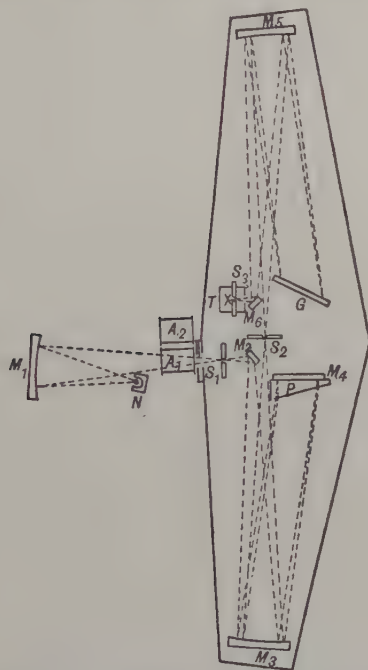


Fig. 32. A refraction and a diffraction spectrometer in tandem. (Sleator.)

A_1, A_2 , Absorption cells; M_1 , Mirror $f=20$ cm.; M_3, M_5 , Mirrors $f=50$ cm.; M_2, M_4, M_6 , Plane mirrors; S_1, S_2, S_3 , Slits; P , Rock-salt prism; N , Nernst glower; G , Reflection grating; T , Thermopile.

in the filtering system. This permits the use of a prism of fairly small angle. Such an apparatus was employed successfully by Sleator and Imes(5), and is shown in Fig. 32. The upper limit of wave-length for which this method would be possible is 23μ (the limit of sylvine transmission), and to extend work further some other means must be sought.

Rubens and Wood(8) devised the plan of focal isolation which is

dependent upon the high refractive index of a material towards waves of frequency less than its natural frequency. They set up a couple of quartz lenses so related to suitable screens that the rays transmitted through the system corresponded to those for which the refractive index of quartz was 2.14. As a result of the two characteristic bands of absorption in quartz at 8.5μ and 20.75μ radiation of wave-length λ greater than 56μ is subject to this high refraction, and it is only such radiation that finds its way through the screens.

This is a development of a method originally used by Rubens and Aschkinass(9) in 1899, in which a small-angled quartz prism was employed as a filter; diaphragms were so placed that waves for which λ was greater than 80μ were transmitted through the system. In order to exclude the radiation of λ less than 4μ , to which the prism was also transparent, a shutter of rock-salt was included in the arrangement. On raising the shutter, which was transparent to waves of wave-length less than 15μ but opaque to longer ones, the extra deflection of the recording instrument was a measure of the intensity of the longer waves. The face of the prism was 6 cms. \times 6 cms., and the angle was about 6° . The thickness of the rock-salt shutter was 4 mm.

Another arrangement is due to Witt(6) who employed a concave grating of the self-focussing Rowland type, and as a radiation filter, two plates, one of quartz and one of rock-salt. When these were used together, the only radiation transmitted had a wave-length shorter than 4μ , whereas, on raising the rock-salt plate, all wave-lengths of λ greater than 50μ were also allowed to pass.

It is interesting to notice that no experimental means have yet been devised for mapping a continuous spectrum between 23μ and 56μ . Isolated portions of the spectrum, such as are produced by the method of Reststrahlen or residual rays can be measured up by the use of an ordinary grating, since in such cases there is no danger of overlapping, but when the whole frequency range is larger than one octave, such a simplification cannot be applied.

In all these methods in which a grating is used for analysis, the

chief difficulty encountered is to ensure a sufficient intensity of diffracted radiation reaching the recording instrument. In contradistinction to a prism which throws all the incident energy into a single spectrum, a grating allows the major portion to enter the geometrical image, while the smaller remainder is distributed among not one, but several, orders of spectra, commonly duplicated on both sides of the optical image.

In this connection it may be useful to observe that R. W. Wood has ruled gratings to which he has given the name of "echelette," and which, on account of the particular shape of the tool used in cutting, throw nearly all the incident energy into one spectrum. These gratings have recently been used in the region of short wave-length ($\lambda < 4\mu$) by Barker⁽⁶⁾ and by Colby, Meyer and Bronk⁽⁶⁾ in their work on the absorption and emission of carbon dioxide and of the absorption of hydrogen chloride respectively.

For work in the longer wave-length region ($\lambda < 50\mu$), similar gratings would be very welcome.

Finally, a way of proceeding in spectral analysis which is independent of prisms or gratings consists in the employment of an interferometer, but this method is clearly restricted to regions of the spectrum for which transparent materials are available. Rubens and Hollnagel⁽¹⁰⁾, and Wood⁽¹¹⁾ have worked with quartz plates for long waves ($\lambda = 70\mu$ to 300μ).

Occasionally it may be impossible to examine the material under test in a continuous spectrum throughout a series of wave-lengths, but instead a series of measurements may be made, in each of which is used a different monochromatic source. This method has been employed by Rubens⁽¹³⁾ and by Laski⁽¹⁴⁾, the radiation being the residual rays from various crystalline substances. By choosing carefully the materials used to produce the beams of Reststrahlen, and by employing a sufficient number of different materials, observations may in this way be extended throughout the spectral range desired. Of necessity the positions along the wave-length scale at which examination may be made are strictly fixed and limited in number.

Photography in the infra-red

Abney⁽¹²⁾ was the first to sensitize and use plates for photography in the infra-red spectrum, but his work scarcely found any application until recently when various workers began to investigate the near infra-red by this means. McLennan⁽¹⁵⁾ has given details of the method of sensitizing ordinary dry plates with dicyanin, which absorbs infra-red radiation and in consequence enables photographs to be taken as far into the spectrum as 1μ with exposures ranging up to thirty hours. On development in the usual manner a negative is obtained of fair density. The method is however tedious, owing to the long exposures necessary, and the range is not extensive. Allibone has used it with success in his investigations of the spectrum of hydrogen, but he only went as far as $\lambda = 0.8349\mu$. (See plate facing p. 37.)

A far preferable method would appear to be that described by Terenin⁽¹⁶⁾ who obtained positives directly. His technique depended upon the fact that a photographic plate when slightly fogged by exposure to visible radiation suffers a reverse change back to the normal condition when irradiated with infra-red. As a result, a line spectrum in the infra-red focussed on to a slightly fogged plate, produces on development of the plate a positive image, bright lines in the spectrum representing strong infra-red radiation. As the infra-red radiation is very largely absorbed in the first or surface layer of the emulsion, the image is lacking in contrast unless the fogging can also be limited to this layer. Consequently he finds it preferable to dye his plates before fogging so that the layer which is fogged and is thus sensitive to the incidence of infra-red radiation is only that lying immediately in the surface.

Terenin recommends using Ilford Monarch or Eastman Super-sensitive plates and treating them, in the dark, with the dye "iodine-green."

Water 100 c.c. Ethyl alcohol 50 c.c.

Aqueous iodine-green 6 c.c. (use 1 in a 1000 solution of the dye).

The plates are soaked in this solution in the dark for five minutes, and the quantities given are enough for about ten quarter-plates. They should then be dried in an air current in the dark for future use, and in this condition will keep for about a month.

The fogging of the plates is effected by illumination by a one or two c.p. glow lamp at a distance of 1 metre for 10 to 20 secs. The plate so fogged is ready for use in the infra-red spectrograph, and should be exposed behind a Wratten filter in order to keep out any trace of ultra-violet radiation. Terenin recommends the use of Wratten Nos. 29 and 45 used together but without a water filter. The time of exposure varies with conditions, but with a good prism spectrograph exposures of 30 minutes to one hour are usual, or if it is desired to push the limit to 1.3μ , two or three hours exposure may be needed. With a grating spectrograph the times must necessarily be increased. To avoid halation backed plates are preferable. Development may be effected by means of any good quick-acting developer, without potassium bromide however, the time being about two or three minutes, and the operation being conducted in absolute darkness.

Receiving Apparatus

In order to measure the intensity of the infra-red rays after passage through the analysing system it is necessary to degrade the electromagnetic energy of radiation into thermal energy in a suitable receiver, and to determine by some convenient means the rise of temperature thus produced.

There are four methods available:

- (a) Bolometer and Wheatstone Bridge,
- (b) Radiometer,
- (c) Thermopile and galvanometer,
- (d) Radiomicrometer.

(a) The Bolometer consists of an extremely thin strip of metal, usually platinum, blackened in order to increase its power of absorption. The resistance forms one arm of a Wheatstone net. When

the radiation is incident upon the bolometer, its temperature and therefore its resistance increase, producing a lack of balance in the bridge with consequent deflection of the galvanometer. The optimum conditions are discussed by Baly(17). An obvious advantage of the bolometer is that it can be constructed with a very narrow strip, so that the radiation collected corresponds almost to that of a single isolated frequency in the spectral band. In all other methods this selection has to be effected by means of a suitable slit placed in front of the receiver.

(b) A Radiometer is based upon the principle underlying the action of the familiar Crookes rotating vane; the force of recoil of the vane warmed by the absorption of radiation and bombarded by the surrounding gaseous molecules is measured by simple torsion of a quartz fibre. The gas pressure for optimum performance is in the neighbourhood of 0.06 mm. of mercury. The details of construction of various types* are given by E. F. Nichols(18) and W. W. Coblentz(19).

An application of the instrument for recent research is being made by Wynn-Williams in the Cavendish Laboratory, Cambridge. He is working with the electromagnetic radiation produced by the method described on p. 111. For detection of such radiation the blackened vanes of the instrument are replaced by short strips of metal sputtered on to the mica. These form electrical oscillators which, resonating in tune with the impressed radiation, absorb and degrade a portion of its energy into thermal form, in consequence of which the vane rotates as usual; see Nichols and Tear(18). A disadvantage of this receiver appears to be its extreme selectivity, necessitating a change of vane whenever the frequency of the radiation is altered.

A drawback to the use of the Nichols type is the excessive time required for the establishment of thermal equilibrium. After admission of the radiation, about 1.5 minutes is required before

* A robust model suitable for general use has lately been perfected by Hettner, and is in use in the Physical Institute of the University of Berlin.

the maximum deflection is obtained. Coblenz states that the instrument is so trustworthy that readings need not be duplicated.

(c) A Thermopile has a great advantage over both the radiometer and the radiomicrometer (see below) in that it may be made light and portable, so that it may, if required, be fixed to the spectrometer arm, a very necessary condition in instruments in which this arm rotates. For accurate work, the thermopile needs to be as sensitive as possible, and not only this, but a galvanometer of the highest sensitivity must be used in conjunction. This involves an additional number of experimental difficulties attendant upon the introduction of a second delicate instrument into the general arrangement. The gain in flexibility, and also in the far greater rapidity of observation, if a suitable galvanometer be chosen, nevertheless outweighs all other disadvantages.

It should be remembered that the recording of the intensity of the radiation depends upon the measurement of the minute E.M.F. set up in the thermopile by the rise of temperature of the junctions. Hence a galvanometer of high voltage-sensitivity is a necessity. The condition for maximum voltage-sensitivity is that the sum of the resistances of the galvanometer and thermopile shall be as low as possible, and because the efficiency of the galvanometer coils increases with the resistance, the optimum working conditions are obtained when the galvanometer resistance is approximately the same as that of the thermopile.

The best means of constructing an efficient thermopile has been discussed by Johansen and Baly⁽¹⁷⁾. It is well known how great an improvement is brought about by working the pile in vacuo, owing to the elimination of heat losses by convection of the surrounding air from the junctions. Moll and Burger⁽²⁰⁾ have shown that under certain conditions the efficiency of a single element may be increased three hundred fold by evacuation.

An ordinary pile is only subject to an increase of sensitivity some three fold, the disparity between the two factors being due

to the conduction of heat in the latter case along the comparatively stout wires of each thermal element in the pile. With a vacuum pile, owing to the absence of convection currents within the container, greatly increased constancy of the galvanometer deflection is experienced. With a pile in air, such inconstancy due to convection currents only becomes noticeable when the deflections are large, and the temperature differences set up within the pile are considerable.

If the instrument is not evacuated, and if the galvanometer is sufficiently sensitive, very large deviations may be observed both in the galvanometer zero and in the deflected reading. These were traced⁽²¹⁾ to unequal heating and cooling of the two junctions of each thermo-element by the minute and continual adiabatic variations in pressure of the surrounding atmosphere.

To avoid these disturbances, all that is required is to enclose the pile in a hermetically sealed container provided with a suitable transparent window for the admission of the radiation.

It is not always convenient to work with a vacuum pile, but the above method provides for the necessary steadiness of the instruments, though naturally it does not pretend to afford the increased sensitivity associated with evacuation. A development along these lines is described in a recent paper⁽²²⁾.

A properly constructed thermopile attains its equilibrium temperature very rapidly after admission of the radiation, and in consequence it is desirable to use a galvanometer of equally rapid action. A second requirement is an instrument which has only a moderate damping coefficient; for this reason, any form of moving coil galvanometer besides having in general a long period for the necessary sensitivity (e.g. about 20 secs.) is disadvantageous because of excessive damping due to the low resistance of the circuit as a whole, e.g. thermopile and galvanometer resistance may each be of resistance 10 to 15 ohms.

On the other hand, a moving magnet instrument, such as one of the Paschen type, suffers from the contrary defect of insufficient

damping, unless indeed the galvanometer be worked in a condition approximating to that of instability.

The following table brings together in a convenient form the important constants relating to several types of galvanometer likely to be used in infra-red work.

High sensitivity Galvanometers

Type	(<i>F.M.</i>)	<i>D</i>	<i>R</i> ohms	<i>T</i> secs.
Moll	2500	4.2	47	1.3
Hill-Downing	19,000	3000	10	8.0
Super-Paschen	20,000	6000	12	12.0

Data calculated from the formula $(F.M.) = (100 DR^{3/5})/T^2$

where (*F.M.*) = Figure of merit.

D = Deflection in millimetres per microvolt, at 1 m.

R = Resistance of coils.

T = Undamped period.

From this it may be seen that the most useful from the point of view of sensitivity is the Paschen type, and for all accurate work it is an essential.

Unfortunately however, by virtue of the extreme lightness of its moving system, it is liable, even more than other patterns, to disturbance by mechanical vibrations. In addition it needs most careful and thorough shielding from stray magnetic fields as well as continual adjustment of its controlling magnets. Soft iron shields prove very inadequate unless assisted by inner shields of Mu-metal or Stalloy. These materials possess a high permeability, if properly annealed, towards fields of very weak intensity. In this respect they differ from soft iron which exhibits feeble permeability for weak fields. Recently the chief instrument makers have taken to providing these shields for their galvanometers.

The important matter of the elimination of mechanical disturbance to the galvanometer will receive attention in a subsequent paragraph.

(d) The well-known Boys' Radiomicrometer consists of a thermojunction and coil, swinging between the poles of a powerful magnet, thus providing in one instrument both receiving and recording devices. Freedom from magnetic disturbance is its outstanding charm: on the other hand its long period (about 30 secs.) militates against rapidity of observation. Like the radiometer already mentioned, this instrument suffers from susceptibility to derangement by stray thermal radiation and by convection currents. Some workers seek to avoid the latter by evacuation of the case, but this can obviously only be undertaken when a suitable window is procurable. In general the instrument must be placed in a compartment separated from the remainder of the apparatus as well as from the observer*.

Since the exit slit of the spectrometer must be comparatively close to the concave reflector by which the receiving plate of the radiomicrometer is irradiated, this isolation of the instrument will probably introduce difficulties connected with the manipulation of the wave-length drum of the spectrometer. A way of surmounting this trouble as well as adding to the speed and convenience of working has been described by one of the present authors⁽²³⁾ who fitted a system of gearing whereby the apparatus was controlled by a positive drive from a distance of fifteen feet.

In order that the room should reach an even temperature, all lamps and the source of infra-red radiation should be lit at least an hour before beginning work. Unfortunately the observer has no immediate control over the position of the coil of the Boys' instrument: the torsion head of the suspension must therefore be set at some position—only to be found by experiment—such that when

* Particular attention should be paid to this point if a modification due to Muselius of Berlin be employed. The modification consists of a highly polished reflecting cone which concentrates the incident radiation upon the vane. The cone, though very efficient as a collector, tends to pick up and magnify the effect of stray radiation.

thermal equilibrium with the surroundings is established, the mirror is suitably orientated.

Owing to the slight nature of the control, the instrument is affected by convection currents within the case, and hence it is usually advisable to read the deflections by means of a telescope and illuminated scale rather than by the usual method of a reflected beam of light.

Elimination of mechanical disturbance

The elimination of mechanical vibration is as important here as in the case of a sensitive galvanometer and of a radiometer. To ensure steadiness in a moving system a first necessity is the coincidence of the centres of gravity and of oscillation. Where this condition holds, in theory at least, small mechanical disturbances should have little or no effect in displacing the spot of light reflected on the scale. In moving-coil instruments a series of trials will enable the experimenter to ensure this state of affairs by means of the addition or subtraction of small portions of wax to the suspended system. Such a method of procedure is not feasible when dealing with such a light and fragile system as that of the Paschen type, and in this case the disturbances must be eliminated at their source.

It has been claimed that a system of box girders affords the maximum rigidity, and in general a structure of this kind is formed by the walls of the laboratory themselves; the galvanometer case may be clamped securely to a vertical wall, or better, to a bracket fixed in the angle between two walls. It is important to choose two very solid walls, preferably the outside walls of the building. Alternatively it may be preferred to use a solid concrete or brick pillar resting directly upon the foundations of the building: the pillar must not be of undue length owing to the tendency to oscillate after the manner of the inverted pendulum.

To minimize the vibrations, should they still be transmitted to the galvanometer case, there are three courses open. The galvanometer may be stood upon a board resting upon (*a*) three tennis

balls, or (b) some hundreds of sheets of brown paper, or (c) three or more thin rubber bags inter-connected and filled with air at a pressure of about 6 or 7 cms. of mercury(24).

Method (a) suffers from the disadvantage of giving the whole system an excessively short and undamped natural period of vibration, and chance tremors tend to maintain it in an almost continuous state of minute disturbance; (b) on the other hand damps out all motions rapidly although it does not entirely prevent disturbances from reaching the instrument; for (c) the originator claims an efficiency of nearly unity.

This arrangement has lately been tested by one of the authors, using four rubber football bladders supporting massive soft iron and Mu-metal shields weighing more than a hundredweight. The air pressure inside the bags (about 6 cms. of mercury) is adjusted until the apparatus is so nearly unstable as to be almost aperiodic. In this condition it is extraordinarily sensitive to minute air currents, but when these are eliminated the freedom of the instrument from mechanical disturbances transmitted from the ground is remarkably good. These methods, though useful in some cases, are not to be recommended. It seems that, when it is possible to stand the galvanometer directly on a bracket fixed between outside walls, there is no better arrangement.

Experimental Method

Actual methods of observation must depend upon a measurement first of the intensity of radiation comprising an extremely narrow range of frequencies, and secondly of the intensity of the same range after the radiation has been transmitted through, or reflected by, the specimen under examination.

Clearly for absorption spectra the experimental arrangement must include a device by which the specimen (crystal slide, liquid cell or gas tube) may be moved in and out of the path of radiation. Care must be taken to ensure that the central ray of the beam passes normally through the substance. Where a cell is used to

contain a liquid or gas a similar empty cell to act as a compensator must be brought into the path of the direct radiation on removal of the specimen. Naturally, the necessity for any kind of cell restricts the region of working on account of the lack of materials transparent between 23μ and 56μ .

It may be noticed that "zaponlack," which is largely composed of cellulose, may become useful for transparent windows in the long wave region. Laski and Tolksdorf(25) have examined its transparency and found that in thin sheets it is possessed of several regions of fair powers of transmission in the long wave spectrum.

In the preparation of crystalline substances, which when possible are cut into thin slices, it is of interest to remark that Tolksdorf(26) has recently performed some experiments upon absorption of crystalline powders in the near infra-red, where, unable to obtain any single crystals from which slices could be cut, she smeared the fine powders between rock-salt plates, in sufficient quantity to produce a milky appearance. This method when further developed should prove of great use, as the trouble encountered in cutting suitably thin films of single crystals is very often considerable and may be quite insurmountable. This is particularly the case with materials which are of importance for theoretical considerations such as those of Goldschmidt(27), and which would well repay investigation in the infra-red.

It should be pointed out that a system of two rock-salt plates, pressed into contact, with a thin film of granular nature between, constitutes a veritable Fabry and Perot interferometer, and consequently the spectra so obtained may not be entirely free from spurious bands due to interference(28). Further examination of this point may be awaited with interest.

In reflection work, the difficulty is to ensure exact replacement of the reflecting surface of the material by the standard reflector (usually silver), as an error of only a few minutes of arc may cause considerable change in the intensity of that portion of the reflected beam received by the slits.

Usually the fraction of intensity transmitted or reflected is the quantity which will be needed for plotting the graph of the spectrum, and this fraction is usually taken to be equal to the ratio of the deflections of the recording instrument. This presupposes a linear relationship between the scale deflection and the intensity of radiation incident upon the receiver, and the choice of the method of reception (radiomicrometer, thermopile, etc.) will be influenced by this consideration. When the ratio of the deflections differs markedly from unity, it is advantageous to insert a diaphragm in the path of the direct beam in order to cut down the larger throw by some constant factor.

The effective intensity of radiation falling upon the receiver is dependent upon the width of the spectrometer slits, and clearly, to obtain maximum resolution, this width must be as small as possible consistent with such a magnitude of deflection as will permit of the desired accuracy of reading.

Owing to the feeble emission of all sources in the far infra-red it will never be necessary to reduce the slit width to such small dimensions that broadening of the spectral bands due to diffraction will take place. Usually it will be found desirable to keep the entrance and exit slits of the spectrometer of equal widths.

There will always be found to be a natural upper limit to the density along the wave-length scale of points of observation. The slit-width should be evaluated in terms of the dispersion of the system. The width of the exit slit is defined as the range of wave-lengths, measured by the drum-setting on the spectrometer, over which strictly monochromatic radiation from an infinitely narrow entrance slit can pass through the exit slit. It will be found that approximately four readings per slit-width as just defined constitute the maximum useful density of points of observation.

To find this slit width throughout the spectrum, it is only necessary to illuminate the entrance slit, which is made as narrow as possible, with some visible monochromatic radiation, e.g. the sodium flame, or the yellow line of neon, which may be obtained from an

Osglim lamp. The rotation of the spectrometer table which is necessary to cause the image of the entrance slit to traverse the width of the exit slit is then determined. From the calibration tables which have already been prepared for the instrument, the difference in wave-length corresponding to this rotation of the table may be found at any required position throughout the spectrum. This wave-length difference is equivalent to the actual width of the exit slit used.

Should it be necessary to work with polarized radiation, use may be made of selenium, which has a constant coefficient of reflection throughout a large spectral range. This indicates that in the infra-red the refractive index is independent of the wave-length, and therefore from Brewster's law, the angle of reflection at which maximum polarization of the radiation occurs is also independent of the wave-length. Experiment shows this angle to be about 70° . Fortunately, selenium may be cast into plane mirrors of considerable size, about 15 cms. \times 5 cms.

A partially polarized beam of radiation can be obtained by a method strictly analogous to the use of tourmaline in the visible spectrum. Any substance, having active vibrations confined to a plane, when prepared in a thin section perpendicular to this plane must partially polarize radiation transmitted normally. The polarization of the transmitted beam is at right angles to the direction of the active vibration. Thus calcite⁽²⁹⁾, when cut into thin slices parallel to the optic axis, partially polarizes the radiation of wave-lengths corresponding to absorption regions. This is particularly the case for the intense bands at about 7.0μ , 11.4μ and 14.1μ .

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MATHEMATICAL APPENDIX

I

Calculation of the molecular moment of inertia J on the basis of classical mechanics and Maxwellian distribution

Lord Rayleigh (1892) showed that if an oscillator which when at rest emits or absorbs radiation of frequency ν_o is set into motion with a rotational frequency ν_r about an axis perpendicular to the plane of vibration (i.e. perpendicular to the figure axis for a diatomic gas molecule), then the frequencies $\nu_o + \nu_r$ and $\nu_o - \nu_r$ should be emitted and absorbed in nearly equal proportions. Thus, let m_1 and m_2 represent the nuclei, the vibrations being supposed to take place along the join m_1m_2 . x, y are orthogonal Cartesian co-ordinates in the plane of the motion, and $\theta = 2\pi\nu_r t$ gives the position of the molecule at the instant t . Now consider the scalar magnitude of the molecular electric moment p . If p is considered periodic in time, then

$$p = A + B \cos 2\pi\nu_o t$$

and the components of this along x and y are

$$\begin{aligned} p_x &= (A + B \cos 2\pi\nu_o t) \cos 2\pi\nu_r t \\ p_y &= (A + B \cos 2\pi\nu_o t) \sin 2\pi\nu_r t \end{aligned}$$

which become

$$\begin{aligned} p_x &= A \cos 2\pi\nu_r t + \frac{B}{2} \left[\cos 2\pi(\nu_o + \nu_r)t + 2\pi(\nu_o - \nu_r)t \right], \\ p_y &= A \sin 2\pi\nu_r t + \frac{B}{2} \left[\sin 2\pi(\nu_o + \nu_r)t - 2\pi(\nu_o - \nu_r)t \right] \end{aligned}$$

respectively, yielding the result already mentioned.

On the basis of a generalized Maxwellian distribution within a group of N molecules in a condition of thermal equilibrium at an absolute temperature T , the number δN having rotational frequencies lying between limits ν_r and $\nu_r + \delta\nu_r$ would be given by

$$\delta N = \frac{4\pi^2 N J}{kT} e^{-\frac{2(\pi\nu_r)^2 J}{kT}} \nu_r \delta\nu_r, \dots\dots\dots(1)$$

where k is Boltzmann's constant ($k = 1.16 \times 10^{-16}$ C.G.S.). From (1), $\frac{\delta N}{\delta \nu_r}$ vanishes for $\nu_r = 0$, and shows a maximum value for $\nu_r = \frac{1}{2\pi} \sqrt{\frac{kT}{J}}$ and thus should give rise to an absorption band which is a doublet having a separation $\delta \nu_r = \frac{1}{\pi} \sqrt{\frac{kT}{J}}$, from which equation J can be obtained if $\delta \nu_r$ is observed. Since J is connected with the inter-nuclear distance a by the equation

$$J = Ma^2 = \left(\frac{m_1 m_2}{m_1 + m_2} \right) a^2 \times 1.64 \times 10^{-24} \text{ C.G.S.},$$

a can be determined. Here M is the reduced mass, $\frac{1}{M} = \frac{1}{m_1} + \frac{1}{m_2}$, m_1 and m_2 are the ordinary atomic weights, 1.64×10^{-24} gms. is the mass of the atom of hydrogen.

II

Pure Rotational Spectrum (older quantum theory)

Corresponding to the treatment in the last paragraph, m_1 , m_2 represent the masses, carrying charges $+e$ and $-e$ at a distance a apart, r_1 and r_2 are the respective distances of m_1 , m_2 from the centre of gravity, and the motion is restricted to one plane.

The kinetic energy U is given by

$$\begin{aligned} U &= \frac{1}{2} (m_1 r_1^2 + m_2 r_2^2) \dot{\phi}^2 \\ &= \frac{1}{2} Ma^2 \dot{\phi}^2, \end{aligned}$$

and p , the moment of momentum of the system, is given by

$$p = \frac{\partial U}{\partial \dot{\phi}} = Ma^2 \dot{\phi} = J \dot{\phi}.$$

Now the total energy $= \frac{1}{2} J \dot{\phi}^2 = H$, (Hamilton's function), so that

$$\begin{aligned} H &= \frac{p^2}{2J} = \alpha_1, \text{ a constant, and } \oint p d\phi = \oint p d\phi = \int_0^{2\pi} \sqrt{2J\alpha_1} d\phi = I \\ &= 2\pi \sqrt{2J\alpha_1} \end{aligned}$$

or

$$\alpha_1 = \frac{I^2}{8\pi^2 J}.$$

The rotational frequency is given by

$$\omega = \frac{\partial H}{\partial I} = \frac{\partial \alpha_1}{\partial I} = \frac{1}{4\pi^2 J}.$$

Introduction of the quantum condition $I = mh$ (m integral) gives the total energy

$$\alpha_1 = \frac{m^2 h^2}{8\pi^2 J},$$

and for a transition $m_1 \rightarrow m_2$

$$h\nu = \alpha_1 - \alpha_2 = \frac{h^2}{8\pi^2 J} (m_1^2 - m_2^2).$$

In emission, for the switch $(m+1) \rightarrow m$,

$$\nu = \frac{h}{8\pi^2 J} \left[(m+1)^2 - m^2 \right] = \frac{h}{8\pi^2 J} (2m+1),$$

which yields a series of lines spaced out at equal distances apart given by

$$\delta\nu = \frac{h}{4\pi^2 J}.$$

The order of magnitude to be expected can be seen by considering the case of HCl. The term $J = Ma^2$ is approximately equal to the mass of the hydrogen atom (1.64×10^{-24} gms.) since the reduced mass is nearly m , and a is known to be not far removed from unity (expressed in Ångströms). Hence, taking $m = 1$

$$\nu \doteq \frac{3 \times 6.55 \times 10^{-27}}{8\pi^2 \times 1.64 \times 10^{-24}},$$

whence

$$\lambda \doteq 200\mu.$$

III

The Planck Oscillator

Type (i). Harmonic.

For simplicity we take first the type in which the motion is assumed to be simple harmonic (force of restitution exactly proportional to the displacements of the nuclei from their positions of

equilibrium). As before, writing the electric moment p periodic in time gives $p_r = p \cos 2\pi(\omega t + \delta)$. The Phase Integral

$$\oint p dq = 2\pi^2 M A^2 \omega$$

(M is the reduced mass, A the amplitude), so that the energy of the system becomes

$$E = \frac{\text{Phase Integral}}{2\pi} \sqrt{\frac{K}{M}}$$

(K is the coefficient of the restoring force per unit displacement). Thus, in the elementary way, the frequency is given by

$$\nu = \frac{1}{2\pi} \sqrt{\frac{K}{M}},$$

from which it appears that the fundamental on a classical or quantum basis is the same. Overtones are excluded because a switch of more than one quantum is forbidden. The frequency of radiation absorbed or emitted coincides with the frequency of vibration.

Type (ii). Anharmonic.

The simple vibrator just considered is inadequate to account for the observed facts, because in a great number of instances harmonics or overtones of the fundamental frequency are found to be present. This can only mean that p contains terms in which such multiple frequencies occur; this again in its turn indicates that the nuclear vibrations are not simple harmonic.

The expansion of the potential function in terms of ascending (negative) powers of the distance between the nuclei has been performed by Sommerfeld (see his *Atomic Structure and Spectral Lines*, Engl. Trans. Brose) and to his work the reader who wishes to study the treatment in detail is referred. Here it may be sufficient to quote the result that the energy in the n th stationary state of such an anharmonic oscillator is given by

$$E_n = n\hbar\omega_0(1 - xn\dots),$$

where

$$x = \frac{\lambda}{4\pi^2 J_0 \omega_0} C_1.$$

Here ω_0 is the natural frequency for very small displacements, J_0 is the moment of inertia which the molecule would possess if it were behaving as a rotator only, and C_1 depends upon particular assumptions upon the nature of the ions (in polar molecules).

The frequencies are easily found from the usual Bohr postulate. Thus the transitions from $n = 1, 2, 3, \dots$ to $n = 0$ are productive of frequencies

$$\omega_0(1-x), \quad 2\omega_0(1-2x), \quad 3\omega_0(1-3x), \dots,$$

so that the overtones should not be exact whole number multiples of the fundamental, a point of great interest to which Kratzer and others have devoted much attention. The above expression, representing the band centres in a system of bands, shows that the interval measured on a frequency scale between successive centres diminishes as the frequency rises. [The reader is referred to the comparison table between old quantum theory and the new Schrödinger mechanics for the way in which the latter modifies the result for the harmonic oscillator. See page 157.]

IV

Rotation-Vibration Spectra (older quantum theory)

Pure rotation and the Planck oscillator having been considered separately, it is possible to couple these effects as already suggested, to account for rotation-vibration bands. This amounts to the recognition that, in a switch giving rise to absorption or emission of radiation, there is a change both in the rotational energy and in the vibrational energy of the molecule. In other words, it is required to introduce a coupling term* y between the energy expressions

$$E_m = Bhm^2 \quad (\text{rotational})$$

$$\text{and} \quad E_n = nh\omega_0(1-xn\dots) \quad (\text{vibrational}).$$

* The practical effect of this coupling term y is to destroy the constancy of $\delta\nu$, which now decreases as ν increases. This is actually observed to occur.

The analysis has been performed by Kratzer, with the result that the energy $E_{n,m}$ ($E_{n,m}$ means the m th rotational state and the n th vibrational state) is given by

$$E_{n,m} = n\hbar\omega_0(1 - xn) + B_0\hbar m^2 - a_n\hbar m^2,$$

where

$$B_0 = \hbar/8\pi^2 J_0,$$

$$a_n = n\hbar^2 y$$

$$= \alpha n,$$

and y is given by

$$y = \frac{3}{32\pi^4 J_0^2 \omega_0} C_2,$$

where the symbols retain their previous meanings, and C_2 is a constant similar to C_1 of the preceding section. m can only change by one unit or zero (the azimuthal angle being cyclic).

Consider a transition (emission) from energy state E_1 to energy state E_2 . There is a decrease in vibrational energy which on Bohr's postulate introduces a term ν_n containing only the vibrational quantum numbers n_1 and n_2 corresponding to E_1 and E_2 . Necessarily there is likewise a term involving m_1 and m_2 and also a term, due to the coupling, involving n_1, n_2, m_1, m_2 . Hence, the final expression for the frequency becomes

$$\nu = \nu_n + B_0(m_1^2 - m_2^2) - (a_{1,n}m_1^2 - a_{2,n}m_2^2).$$

An unchanged value of m is excluded unless the molecule possesses an electric moment perpendicular to the plane of rotation. Thus $m_1 = m_2 \pm 1$. Since ω_0 is numerically large compared with B_0 (see previous equations) we can neglect y , and

$$\nu = \nu_n + B_0(2m_2 + 1) \quad (E_m \text{ decreases}),$$

or

$$\nu = \nu_n + B_0(-2m_2 + 1) \quad (E_m \text{ increases}),$$

to a first approximation. The first of these gives the so-called positive branch, generally denoted by R , and the second the negative branch denoted by P . If m is zero we have $\nu = \nu_n + B_0$, which may be called the zero branch. It bisects the distance between the first line of the R branch and the first line of the P branch. The P and R branches are symmetrical about it, but it is not

coincident with the vibrational frequency ν_n . If the rotational quantum number does not change, i.e. if $\Delta m = 0$, then $\nu = \nu_n$ and this may be called the *Q* branch, according to the usual habit in ultra-violet band spectra. The transition is, as mentioned, only permitted in certain cases. The frequency interval between adjacent lines in both the *P* and *R* branches is, for this treatment which ignores y , constant, and the same as for a pure rotation spectrum. This important result has been mentioned before, and enables moments of inertia to be found in the same way from rotation-vibration bands as from those due to pure rotation. It may be helpful to remember that if frequencies are plotted graphically, with ν increasing towards the right, then the *R* branch is to the right of the centre, and the *P* branch to the left. The anomaly of the centre of the band system not coinciding with ν_n , the vibrational frequency, is removed by the introduction of half quantum numbers into the treatment. When this is done the zero or null branch becomes identical with the *Q* branch.

V

SCHRÖDINGER'S WAVE MECHANICS

Introductory

Within the last few years it has become increasingly clear that Newtonian mechanics, even assisted when necessary with relativistic refinements, are incapable of describing the states of molecular and atomic systems. In other words, the quantum theory needed a new mechanics suitable for systems of the order of magnitude met with in modern physical research.

The first attempt in this direction was due to Heisenberg, and resulted (the mathematical machinery being in part due to Born and Jordan) in the matrix mechanics. The basic idea was that only directly observable quantities such as intensity and frequency

should find place in a rational theoretical physics, and thus the possibility of knowing the history of an electron in a stationary state (i.e. where it does not radiate) was frankly abandoned.

Meanwhile, L. de Broglie was following up a totally different line of enquiry founded essentially upon the principle of Fermat, and a consideration of its close analogy with the well-known "extremum" of Maupertuis and Euler.

The two integrals may be written

$$\int_A^B \frac{ds}{u} = \text{Minimum} \quad [\text{Fermat}] \dots\dots\dots(\text{i})$$

(ds = element of length along the path AB , u = wave velocity of a light ray from A to B),

$$\int_A^B v ds = \text{Minimum}^* \quad [\text{Maupertuis-Euler}] \dots\dots(\text{ii})$$

(v = mechanical velocity of a particle from A to B). Thus the mechanical velocity v in the second integral corresponds to the reciprocal wave-velocity in the first, and suggests the possibility of describing mechanical processes by the theory of wave motions.

A wave group is next considered. By a wave group is meant a number of waves of which the frequency within a certain region differs from member to member of the group. At a certain position within such a group, the energy density will reach a maximum, and this position may be termed the energy centre of the group. This energy centre may then be conceived as moving forward with a certain velocity g (the group velocity) which is accordingly the velocity with which the energy associated with the waves of the group spreads out.

If now, as a fundamental conception, a wave motion is accepted as inseparable from the mechanical motion of a material particle, it is possible to deduce the conditions that the group velocity g of

* Strictly, this integral might alternatively be a maximum; all that theory requires is an "extremum."

the former agrees with the mechanical velocity v of the latter; i.e. it is required that

$$g = v. \dots\dots\dots(\text{iii})$$

Considerations of this nature prompted Schrödinger to ask whether it was not possible to deal with molecular and atomic phenomena by methods involving, for the most part, the highly developed machinery of differential equations. Virtually the problem of quantization is reduced to that of finding suitable solutions to equations which are of the general type of (6) discussed later. He brought forward the far-reaching analogy between the transition from geometrical optics to wave optics and that from classical particle mechanics to a "wave mechanics."

Thus, in the same way that it becomes unjustifiable to apply the methods of geometrical optics when obstacles and apertures become comparable in their dimensions with the wave-length, Schrödinger considers the breakdown of particle mechanics for distances of the order of molecular or atomic dimensions. This view ascribes the failure of the cruder treatment in both cases to the fact that both light and matter originate in wave motions (compare equation $g = v$ above).

Consider next the usual Laplacian expression (in Cartesian co-ordinates)

$$\nabla^2 S = \frac{\partial^2 S}{\partial x^2} + \frac{\partial^2 S}{\partial y^2} + \frac{\partial^2 S}{\partial z^2}, \dots\dots\dots(\text{iv})$$

where S is a physical magnitude such that its second time derivative is proportional to $\nabla^2 S$, i.e.

$$\frac{\partial^2 S}{\partial t^2} = \sqrt{k} \nabla^2 S,$$

and which, as in the usual theory of wave motion, always gives the possibility of the quantity S spreading out with velocity $u = \sqrt{k}$, in which u represents the wave velocity as before.

If a purely sinusoidal oscillation be considered, then $\frac{\partial^2 S}{\partial t^2}$ may

be written equal to $-4\pi^2\nu^2S$, and on substitution in (iv) there results

$$\nabla^2 S + 4\pi^2\nu^2 S/u^2 = 0. \dots\dots\dots(v)$$

Also, de Broglie's relationship between the frequency ν and the momentum for a single particle leads to the equation

$$\nu^2/u^2 = (mv/h)^2 = (2m/h^2) mv^2/2,$$

where the kinetic energy $mv^2/2$ is equal to the difference between the total energy E and the potential energy V . If this value be substituted for ν^2/u^2 in (v), then

$$\nabla^2 S + \frac{8\pi^2m}{h^2} (E - V) S = 0 \dots\dots\dots(vi)$$

and this is the fundamental equation of Schrödinger's theory.

Schrödinger, using the operator calculus, has also shown that, although developed from such widely different conceptions, the wave mechanics and the matrix treatment of Heisenberg-Born-Jordan are mathematically identical.

Special Problems

The list of papers and books (in English) given on page 158 should be consulted for details of a more mathematical nature. The following is an outline of special cases met with in this book.

The wave equation

$$\text{Div grad } \psi + \frac{8\pi^2m}{h^2} (E - V) \psi = 0, \dots\dots\dots(1)$$

or, if the form $\nabla^2 \equiv \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$ is preferred, then (1) may be written

$$\nabla^2 \psi + \frac{8\pi^2m}{h^2} (E - V) \psi = 0. \dots\dots\dots(2)$$

Here V is the potential energy, E —or in particular E_n —represents the series of energy levels in the quantum sense which it is usually sought to determine.

ψ is more difficult to conceive—for many purposes it is needless to attach to it a physical meaning, but if one is required, then Schrödinger suggests that the definition

$$\psi\bar{\psi} = \text{the electric density}$$

be accepted.

$\bar{\psi}$ is the conjugate of the complex quantity ψ

[e.g. if $\psi = Ae^{ixt}$ where A is real

and $\bar{\psi} = Ae^{-ixt}$,

then the electric density $\psi\bar{\psi} = A^2$].

The idea is that if ψ vibrates originally with frequency E_1/h , and finally with frequency E_2/h , then the frequency of emitted radiation is the beat frequency of these two. Perhaps the simplest way to proceed is to separate equation (2) into its essentials for the present particular purpose. These essentials are (a) the term V ; (b) the term E ; (c) the term ψ , and they will be discussed in this order.

(a) The term V

Generalized co-ordinates, p, q , where p is the conjugate momentum and q the positional co-ordinate, are usually employed to express V . The co-ordinate q is a length or an angle as the case may be. Thus, for convenience, V may be written as $V(q)$ to keep this point in the foreground. This expression of V in terms of q can usually be made on beginning work at the particular problem (e.g. for an harmonic oscillator $V(q) = 2\pi^2\nu_0^2q^2m$ in the ordinary way, where ν_0 is the fundamental frequency and q the displacement of the particle from the equilibrium position).

(b) The term E and (c) the term ψ

A consideration of the term E is hardly possible without some reference to ψ . Schrödinger investigates the conditions necessitated by the requirement that the solution of (2) shall be finite, continuous, and single-valued. By this is meant that ψ , the argument,

shall be finite, continuous, and single-valued, and the result of this restriction is found to be that E can only assume certain discrete values depending upon whole numbers. These particular values of E are called in German *Eigenwerte*, and the solutions ψ which satisfy the above conditions are known as *Eigenfunktionen*. Since no convenient words exist in English to convey these meanings the German renderings will be used.

The general method of proceeding can now be outlined.

First step. Form the potential energy $V(q)$ and insert this for V in equation (2). This immediately leads to the appropriate wave equation for the particular problem.

Second step. Recognize the solutions of this equation to satisfy the conditions. Like any other standard differential equation, the equation (2) is solved by recognizing the equation from which it is derived*.

The following particular cases may be considered—not necessarily all in detail, where the work would become unduly complicated.

- (A) The Planck oscillator.
- (B) The rotator with fixed axis.
- (C) The rigid rotator with free axis.
- (D) The dumb-bell, i.e. a diatomic molecule.

A merit of the wave mechanics is that it affords a direct calculation of the intensities of spectra. From the expression for electric density $\psi\bar{\psi}$, the electric moment of the system is obtained by integration, after which purely classical conceptions avail for determining the characteristics of the radiation.

* For example: The solution of Bessel's equation is known to be given by the Bessel functions, which have been tabulated over a wide range of numerical values because of their great importance in analytical dynamics.

Again, spherical harmonics assume an outstanding position in electrostatics because of the solution which they offer of the equation of Laplace, $\nabla^2 V = 0$. The purpose of this note is to convey the impression that a similar method of treating Schrödinger's wave equation is the accepted one.

(A) *The Planck Oscillator*

If ν_0 is the fundamental frequency of vibration of an oscillator of mass m and displacement q , then, as usual,

$$V(q) = 2\pi^2\nu_0^2mq^2 \dots\dots\dots(3)$$

and corresponds to the first step in the last paragraph. Introduction of (3) into the fundamental wave-equation (2), yields

$$\frac{d^2\psi}{dq^2} + \frac{8\pi^2m}{h^2}(E - 2\pi^2\nu_0^2q^2)\psi = 0, \dots\dots\dots(2')$$

or, for convenience, if

$$a = \frac{8\pi^2Em}{h^2},$$

$$b = \frac{16\pi^4\nu_0^2m^2}{h^2},$$

then

$$\frac{d^2\psi}{dq^2} + (a - bq^2)\psi = 0.$$

A new independent variable $y = q\sqrt[4]{b}$ transforms this into

$$\frac{d^2\psi}{dy^2} + \left(\frac{a}{\sqrt{b}} - y^2\right)\psi = 0, \dots\dots\dots(2'')$$

an equation of which both the Eigenwerte and Eigenfunktionen are well known. The former are given by the series of discrete values

$$\frac{a}{\sqrt{b}} = 1, 3, 5, \dots(2n+1), \dots\dots\dots(4)$$

and the latter by the Hermitic Orthogonal functions $e^{-\frac{y^2}{2}}H_n(y)$. Here $H_n(y)$ means the n th polynomial, which can be defined as

$$H_n(y) = (-1)^n e^{y^2} \frac{d}{dy^n} e^{-y^2}.$$

The first few members of the series are easily found. They are

$$H_0(y) = 1.$$

$$H_1(y) = 2y.$$

$$H_2(y) = 4y^2 - 2.$$

Using the relation already given for a and b together with equation (4), and writing E_n for E , we find that

$$E_n = \frac{2n+1}{2} h\nu_0,$$

or $E_n = (n + \frac{1}{2}) h\nu_0, \dots\dots\dots (5)$

giving the energy E_n in the n th stationary state ($n = 0, 1, 2, \dots$).

The Eigenfunktionen $e^{-\frac{y^2}{2}} H_n(y)$ are the solutions of ψ in the funda-

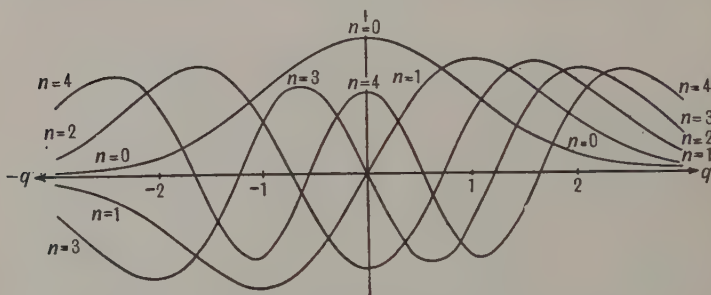


Fig. 33. Forms of ψ for different values of n . (Darrow.)

mental equation (2''). If it is remembered that $y = q \sqrt[4]{b}$, and that

$$b = \frac{16\pi^4 \nu_0^2 m^2}{h^2},$$

then

$$y^2 = q^2 m \frac{4\pi^2 \nu_0}{h},$$

and thus

$$\psi_n = e^{-2\pi^2 \nu_0 m q^2 / h} \cdot H_n \left(2\pi q \sqrt{\frac{m\nu_0}{h}} \right),$$

and consequently

$$\psi_0 = e^{-2\pi^2 \nu_0 m q^2 / h},$$

$$\psi_1 = 8\pi q \sqrt{\frac{m\nu_0}{h}} \cdot e^{-2\pi^2 \nu_0 m q^2 / h},$$

and so on.

ψ_0 is a Gauss "error curve"; ψ_1 vanishes at the origin, and represents (q positive) a Maxwellian distribution in a plane: it has

one finite node at $q = 0$, whereas ψ_0 never vanishes and the corresponding wave is therefore of infinite length.

Equation (5) shows that the energy levels follow a series of odd multiples of $\frac{h\nu_0}{2}$, but the differences of levels—with which radiation is concerned—are the same as on the older theory. Apart from questions of a zero-point energy, the term $\frac{h\nu_0}{2}$ influences the rules dealing with band edges in spectral series.

(B) *The Rotator with fixed axis*

For the present purpose, this case is exceedingly simple, for there is no potential energy term.

If ϕ is the angle giving the rotation at time t and J the moment of inertia about an axis perpendicular to the axis of figure, then the fundamental wave-equation takes the form

$$\frac{d^2\psi}{dq^2} + \frac{8\pi^2 Em}{h^2} \psi = 0.$$

Transformation into polar co-ordinates (ϕ, r) and substitution of $J = mr^2$ gives

$$\frac{1}{J} \frac{d^2\psi}{d\phi^2} + \frac{8\pi^2 E}{h^2} \psi = 0, \quad \dots\dots\dots(2''')$$

which has the well-known solution

$$\psi = \frac{\sin}{\cos} \left\{ \sqrt{\frac{8\pi^2 EJ}{h^2}} \phi \right\}. \quad \dots\dots\dots(6)$$

ψ must be equal to whole number multiples of ϕ , in order to attain uniqueness and continuity, and hence

$$E_n = \frac{n^2 h^2}{8\pi^2 J} \quad \dots\dots\dots(7)$$

in complete agreement with the older theory.

(C) *The Rigid Rotator with free axis*

If (ϑ, ϕ) are the polar co-ordinates of the figure axis, then the kinetic energy can be expressed as a function of the momenta as follows:

$$T = \frac{1}{2J} \left(p_{\vartheta}^2 + \frac{p_{\phi}^2}{\sin^2 \vartheta} \right),$$

which is of the form assumed by the kinetic energy equation of a mass-point constrained to move upon a spherical surface.

The fundamental equation of Schrödinger thus becomes

$$\frac{1}{\sin \vartheta} \frac{\partial}{\partial \vartheta} \left(\sin \vartheta \frac{\partial \psi}{\partial \vartheta} \right) + \frac{1}{\sin^2 \vartheta} \frac{\partial^2 \psi}{\partial \phi^2} + \frac{8\pi^2 J E}{h^2} \psi = 0 \quad \dots (2^{iv})$$

(see any book on transformation of co-ordinates for this purely formal step).

The condition that ψ on the spherical surface shall be single-valued and continuous, leads at once to the Eigenwerte

$$\frac{8\pi^2 J}{h^2} E = n(n+1), \quad n = 0, 1, 2, \dots$$

or, in particular,
$$E_n = \frac{n(n+1)h^2}{8\pi^2 J} \dots \dots \dots (8)$$

for the energy levels (compared with $\frac{n^2 h^2}{8\pi^2 J}$ on the older theory).

(D) *The Dumb-bell model, i.e. Diatomic molecule*

The two nuclei m_1, m_2 , at a distance r apart have Cartesian co-ordinates (x_1, y_1, z_1) and (x_2, y_2, z_2) . The potential energy V is thus

$$V = 2\pi^2 \nu_0^2 M (r - r_0)^2,$$

where M is the reduced mass as before and r_0 the distance apart for minimum potential energy, and

$$r = \{(x_1 - x_2)^2 + (y_1 - y_2)^2 + (z_1 - z_2)^2\}^{\frac{1}{2}}.$$

ν_0 is the fundamental vibration frequency of m_1, m_2 in the absence of rotation.

The wave-equation thus becomes

$$\frac{1}{m_1} \left(\frac{\partial^2 \psi}{\partial x_1^2} + \frac{\partial^2 \psi}{\partial y_1^2} + \frac{\partial^2 \psi}{\partial z_1^2} \right) + \frac{1}{m_2} \left(\frac{\partial^2 \psi}{\partial x_2^2} + \frac{\partial^2 \psi}{\partial y_2^2} + \frac{\partial^2 \psi}{\partial z_2^2} \right) + \frac{8\pi^2}{h^2} \{E - 2\pi^2 \nu_0^2 M (r - r_0)^2\} \psi = 0. \dots (2v)$$

A somewhat lengthy analysis leads to the following expression for the energy levels

$$E = E_t + \frac{n(n+1)h^2}{8\pi^2 J} \left(1 - \frac{\epsilon}{1+3\epsilon} \right) + \frac{2l+1}{2} h\nu_0 \sqrt{1+3\epsilon}, \quad (9)$$

$$n = 0, 1, 2, \dots \quad l = 0, 1, 2, \dots,$$

where E_t is the translational energy, and

$$\epsilon = \frac{n(n+1)h^2}{16\pi^4 \nu_0^2 J^2} \quad (J = Mr_0^2).$$

The result is similar to that on the older theory except that half quantum numbers occur throughout.

Energy Levels E_n

NEW	OLD
Planck oscillator $(n+1/2)h\nu_0$ $n=0, 1, 2, 3, \dots$	$nh\nu_0$
Rigid rotator with free axis $n(n+1)h^2/8\pi^2 J$ $n=0, 1, 2, 3, \dots$	$n^2 h^2 / 8\pi^2 J$
Rotator with fixed axis $n^2 h^2 / 8\pi^2 J$ for both $n=0, 1, 2, 3, \dots$	
Dumb-bell Model Same for both, except half quanta throughout in the new.	

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VI

The Dispersion of CO₂

Fuchs(1) compares the experimental values due to a number of investigators with a dispersion curve, based on the classical theory of dispersion, which, with suitably chosen constants, represents the variation of refractive index n of this gas from the ultra-violet to 13μ .

The form of the equation is the usual one if we write

$$\frac{n^2 - 1}{n^2 + 2} = \frac{2}{3}(n - 1),$$

since n is very nearly unity.

Thus
$$n - 1 = \sum_i \frac{C_i}{\nu_i^2 - \nu^2},$$

when

$$C_i = \frac{Ne^2 p_i}{2\pi};$$

p is, according to classical conceptions, the number of effective oscillators at the i^{th} frequency ν_i whereas on the quantum theory p is connected with the transition probability coefficients. N is the number of molecules per cm.³, and m the mass (see later). Insertion

of the constants to obtain the closest agreement with observation leads to the formula

$$n-1 = \frac{7.3205 \times 10^{27}}{17341.6 \times 10^{27} - \nu^2} + \frac{8.2060 \times 10^{25}}{4108.8 \times 10^{27} - \nu^2} \\ + \frac{1.1676 \times 10^{23}}{4.845 \times 10^{27} - \nu^2} + \frac{8.1742 \times 10^{21}}{0.405 \times 10^{27} - \nu^2}.$$

The infra-red wave-lengths (in Fuchs' notation) are

$$\lambda_3 = 4.31\mu \text{ and } \lambda_4 = 14.91\mu,$$

whilst the corresponding p values are

$$p_3 = 1.729,$$

$$p_4 = 0.121.$$

The factor m is taken, in the ultra-violet, as the mass of the electron; in the infra-red as the reduced mass for CO_2 .

A consideration of the ratio of the intensities for λ_3 and λ_4 leads to a value distinctly too high compared with the results of Schaefer and Philipps' (2) absorption curves. Extrapolation of the formula for $\lambda = \infty$, yields the figures 1.000975 for the dielectric constant, agreeing excellently with Zahn's (3) experimental result

$$\epsilon = 1.000976.$$

VII

The CO_3^{--} group (classical mechanics).

The potential energy ϕ of the CO_3^{--} group, assumed as an ionic complex in the form of a plane equilateral triangle, can be deduced as the sum of a series of terms. If the CO_3^{--} group is made up of a charge $4e$ on the carbon and $-2e$ on each oxygen, then the electrostatic potential is composed of two parts.

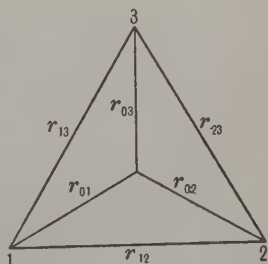


Fig. 34.

(i) The potential of the O^{--} 's in the field of the C^{+++} which amounts to $-4e \sum_{\kappa=1}^3 \frac{2e}{r_{0\kappa}}$.

(ii) The potential of any one O^{--} in the field of the others amounting to $2e \left\{ \frac{2e}{r_{12}} + \frac{2e}{r_{23}} + \frac{2e}{r_{31}} \right\}$.

To insure stability, it is necessary to assume a repulsive force between the ions, and Kornfeld(4) supposes the law to be of the form $\frac{be^2}{r^5}$ for the potential.

(iii) Consideration of the repulsion between the O's and the C's introduces a term $be^2 \sum_{\kappa=1}^{\kappa=3} \frac{1}{r_{0\kappa}^5}$ into the potential function. The repulsive potential between the O's is neglected.

As a result of the deformability of the electronic shells, dipoles of moment \mathbf{p} are set up in each ion, according to the equation

$$\mathbf{p} = \alpha \mathbf{E},$$

where α is a constant characteristic of the ion, and \mathbf{E} is the inducing electric field. The deformability of carbon is negligible compared with that for oxygen. The contribution made to the potential function on account of this effect consists of three parts:—

(iv) The quasi-elastic energy of the dipole.

The energy F of a dipole in field \mathbf{E} is equal to \mathbf{pE} , whence $dF = \mathbf{p}d\mathbf{E}$, or since $\mathbf{p} = \alpha \mathbf{E}$, $\therefore dF = \alpha \mathbf{E}d\mathbf{E}$.

$$\text{Integrating,} \quad F = \alpha \int_0^{\mathbf{E}} \mathbf{E}d\mathbf{E} = \frac{1}{2} \alpha \mathbf{E}^2 = \frac{1}{2} \frac{\mathbf{p}^2}{\alpha}.$$

The total quasi-elastic energy of the three deformed O ions is

$$\frac{1}{2\alpha} \sum_{\kappa=1}^{\kappa=3} \mathbf{p}_{\kappa}^2.$$

(v) The field produced by these induced dipoles reacts upon the C ion and alters its potential. A charge e distant r from a dipole of moment \mathbf{p} has an energy $\frac{e\mathbf{p}}{r^2}$, and therefore the C ion is subject to an alteration of potential of amount

$$4e \sum_{\kappa=1}^{\kappa=3} \frac{\mathbf{p}_{\kappa}}{r_{0\kappa}^2}.$$

(vi) Finally the potential of each O ion is altered by the reaction of the neighbouring induced dipoles.

The sum of this effect is

$$2e \sum_{\substack{\kappa=3 \\ \kappa, \kappa'=1 \\ \kappa' \neq \kappa}} \frac{\mathbf{p}_{\kappa}}{r_{\kappa'\kappa}^2}.$$

Adding these six terms, and having regard to sign, we have

$$\begin{aligned} \phi = & -4e \sum_{\kappa=1}^{\kappa=3} \frac{2e}{r_{0\kappa}} + 2e \left\{ \frac{2e}{r_{12}} + \frac{2e}{r_{23}} + \frac{2e}{r_{31}} \right\} + be^2 \sum_{\kappa=1}^{\kappa=3} \frac{1}{r_{0\kappa}^5} \\ & + \frac{1}{2\alpha} \sum_{\kappa=1}^{\kappa=3} \mathbf{p}_{\kappa}^2 - 4e \sum_{\kappa=1}^{\kappa=3} \frac{\mathbf{p}_{\kappa}}{r_{0\kappa}^2} + 2e \sum_{\substack{\kappa, \kappa'=1 \\ \kappa \neq \kappa'}}^{\kappa=3} \frac{\mathbf{p}_{\kappa}}{r_{\kappa'\kappa}^2}. \dots\dots(1) \end{aligned}$$

The solution of this equation can be found in the original paper: the analysis is too complicated for reproduction here.

The quartic equation giving two of the natural frequencies is a function of the masses, as well as the parameters in the above expression for ϕ . It follows that these two frequencies are double, and by the insertion of the appropriate values, Kornfeld finds the corresponding wave-lengths to be

$$6.5\mu,$$

$$16.3\mu,$$

whereas the observed figures are (for calcite) more nearly

$$6.7\mu,$$

$$14.2\mu.$$

The theoretical treatment gives these two vibrations polarized in the plane of the group as experiment requires.

Corresponding equations for the other two solutions give an active frequency polarized in a direction perpendicular to that of the last two, at a wave-length of 10.4μ , and an inactive one at 7.42μ . [In Kornfeld's paper, he presents the solutions in terms of ω , where $\omega = 2\pi\nu = \frac{2\pi c}{\lambda}$.] Schaefer⁽⁵⁾ finds, for the frequency polar-

ized at right angles to the plane of the CO_3 group, a wave-length of 11.38μ for calcite.

This treatment is purely ideal, as it only considers the CO_3^{--} group as an isolated unit, whereas observation shows a marked influence of the surrounding lattice.

An equation analogous to (1) can be constructed for ϕ to give the potential of any lattice configuration of ionic charges, and for the SO_4^{--} group this has been solved by Rolan(6).

VIII

Einstein's (7) Frequency Formula

The basic supposition is that the characteristic frequency ν is a function of the mass m of the vibrations, d their distance apart, and the compressibility κ of the crystal.

In general then, $\nu = C \cdot m^x \cdot d^y \cdot \kappa^z$,

whence inserting the dimensions of ν , m , d , κ it appears that

$$[T]^{-1} = C [M]^{x-z} [L]^{y+z} [T]^{2z},$$

or equating the indices

$$\left. \begin{aligned} x - z &= 0 \\ y + z &= 0 \\ 2z &= -1 \end{aligned} \right\},$$

whence

$$\nu = C m^{-\frac{1}{2}} d^{\frac{1}{2}} \kappa^{-\frac{1}{2}}.$$

For a cubic lattice (edge = d) the density ρ is given by $\rho = m/d^3$ ($m = A/N$ if A is the atomic weight and $N = 6.06 \times 10^{23}$).

Thus, $\nu = C' \kappa^{-\frac{1}{2}} A^{-\frac{1}{3}} \rho^{-\frac{1}{6}}$.

Einstein fixes C' by taking the influence of twenty-six neighbouring atoms upon the atom supposed to be vibrating with frequency ν .

Grüneisen's Frequency Formula

Einstein's frequency formula can be written in the form

$$\nu_0 = c \kappa^{-\frac{1}{2}} M^{-\frac{1}{3}} \rho^{-\frac{1}{6}}, \dots \dots \dots (1)$$

where the suffix means the absolute zero of temperature. On the basis of the virial theorem of Clausius, the equation of state of a solid can be written in the form

$$pV + G(V) = \gamma \cdot 2\bar{L}, \dots\dots\dots(2)$$

where p is the external pressure; V the volume; \bar{L} is the statistical value of the kinetic energy; γ is—for the present purpose—a constant; $G(V)$ depends upon the law of force assumed to control the lattice (i.e. the law of force is a function of r , the distance between atoms in the lattice, and V clearly depends upon r^3 ; hence V depends upon the law of force).

Also, the compressibility κ_0 is connected with $G(V)$ by the relation

$$\frac{1}{\kappa_0} = \left[\frac{d}{dV} G(V) \right]_0. \dots\dots\dots(3)$$

For $p=0$, it is possible to find the thermal expansion α by an approximate solution of the equation

$$G(V) = \gamma \cdot 2\bar{L}, \dots\dots\dots(4)$$

which, since C_v , the specific heat at constant volume, is equal to

$\frac{\partial}{\partial T} (2\bar{L})_v$, leads to the expression

$$\frac{C_v}{3\alpha} = \frac{V_0}{\gamma \kappa_0}, \dots\dots\dots(5)$$

or

$$\kappa_0 = \frac{3\alpha}{C_v} \frac{\gamma}{V_0}. \dots\dots\dots(6)$$

Insertion of this value for κ_0 into (1) gives

$$\nu_0 = c' \sqrt{\frac{C_v}{MV^{\frac{2}{3}} 3\alpha}}, \dots\dots\dots(7)$$

where c' is a new constant. The constant c' is determined empirically, and amounts to 2.9×10^{11} .

Hence, Grüneisen's formula can be written

$$\nu_0 = 2.9 \times 10^{11} \sqrt{\frac{C_v}{MV^{\frac{2}{3}} 3\alpha}} \dots\dots\dots(8)$$

or sometimes, since it is only applicable to monatomic bodies, A is written as the atomic weight instead of M , and the density ρ retained instead of the volume. In this case, the result is

$$\nu_0 = 2.9 \times 10^{11} A^{-\frac{5}{6}} \left[C_v^{\frac{1}{2}} \alpha^{-\frac{1}{2}} \rho^{\frac{1}{3}} \right]_0. \dots\dots\dots(9)$$

Debye's Frequency Formula

It is well known (see Reiche's *Quantum Theory*, or Jeans' *Dynamical Theory of Gases*) that in a continuum, the number of natural periods of frequency lying between ν and $\nu + d\nu$ is given by

$$Z(\nu) d\nu = 4\pi V \left(\frac{1}{c_l^3} + \frac{2}{c_t^3} \right) \nu^2 d\nu,$$

where V is the volume of the solid, and c_l and c_t are the velocities of sound longitudinally and transversely through the body. If we stop at the $3N$ th natural period, there is found the greatest frequency ν_{\max} occurring in the elastic spectrum. It is obtained by integrating the above expression between the limits $\nu = 0$ and $\nu = \nu_{\max}$ and setting the result equal to $3N$.

$$\text{Then} \quad \nu_{\max} = \left[\frac{9N}{4\pi V \left(\frac{1}{c_l^3} + \frac{2}{c_t^3} \right)} \right]^{\frac{1}{3}}. \dots\dots\dots(10)$$

A drawback to this formula is that it does not contain quantities directly capable of measurement. This can be overcome by noting (see any text-book on the theory of elasticity) that

$$c_l = \left[\frac{3(1 - \sigma)}{(1 + \sigma)\kappa\rho} \right]^{\frac{1}{2}},$$

$$\text{and} \quad c_t = \left[\frac{3(1 - 2\sigma)}{2(1 + \sigma)\kappa\rho} \right]^{\frac{1}{2}},$$

where κ is the compressibility, σ Poisson's ratio, and ρ the density. Also $V = \frac{A}{\rho}$, where A is the atomic weight. Hence, by substituting these values in (10), we have

$$\nu_{\max} = \frac{5.28 \times 10^7 f(\sigma)}{A^{\frac{1}{3}} \rho^{\frac{1}{3}} \kappa^{\frac{1}{2}}},$$

where
$$f(\sigma) = \left\{ \frac{2}{3} \left[\frac{2(1+\sigma)}{3(1-2\sigma)} \right]^{\frac{3}{2}} + \frac{1}{3} \left[\frac{1+\sigma}{3(1-\sigma)} \right]^{\frac{3}{2}} \right\}^{-\frac{1}{2}}.$$

Braunbek's (8) Frequency Formula

The reciprocal potential of two lattice particles in a crystal is assumed to be periodic, and of the form

$$f(u) = A \sin^2 \frac{\pi u}{s},$$

where u is the displacement, and s the wave-length of this periodic potential.

The following are the main features of the theory relevant to the establishment of a frequency formula.

(1) The mean kinetic energy \bar{L} of the system is calculated as a function of the total energy E , i.e. $\bar{L} = \phi(E)$.

(2) For \bar{L} is written $n \cdot \frac{3}{2} R$, where n is the number of atoms in the molecule and R the gas constant.

(3) E is now identified with U , the internal energy of the crystal.

The relationship between \bar{L} (or $n \cdot \frac{3}{2} R$) and E (or U) is shown by the accompanying graph (Fig. 35) where the curve is cut in three points by a horizontal straight line BCD . B corresponds to the solid phase, D to the fluid, whereas C is labile.

The position of this straight line is fixed by the condition *

$$\oint \frac{dU}{T} = 0.$$

* Braunbek considers an imaginary reversible cycle, in which the starting-point is B , thence along the curve to E , thence via the unstable section ECF

(BD) is a measure of the heat of melting (calculated per mol), and the ordinate (BJ) a measure of the melting-point temperature.

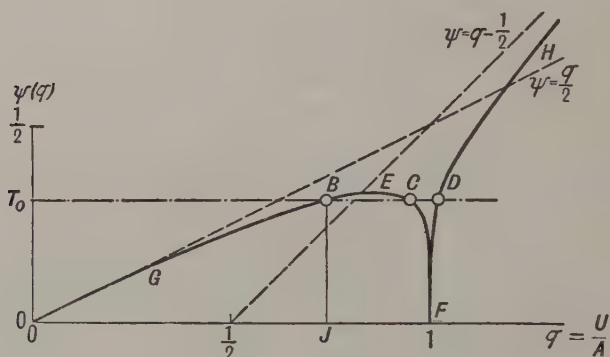


Fig. 35. The form of the function $\psi\left(\frac{U}{A}\right)$, (Braunbek).

From the form of the function, the quantities (BJ) and (BD) can be evaluated as absolute constants, yielding

$$(BJ) = 0.310,$$

$$(BD) = 0.276,$$

and a relationship obtained (on the basis of the periodic potential $A \sin^2 \frac{\pi u}{s}$) between the natural frequency of oscillation ν and the melting-point temperature.

The final form of this relationship is

$$\nu = \left\{ \frac{1}{2x} \left(\sqrt{\frac{M_1}{M_2}} + \sqrt{\frac{M_2}{M_1}} \right) \sqrt{\frac{3nR}{(BJ)}} \sqrt[3]{N} \right\} \sqrt{\frac{T_{sm}}{M \cdot v_m^{\frac{2}{3}}}}.$$

In this expression M_1 and M_2 are the atomic weights, M the molecular weight, N is Avogadro's number, T_{sm} the melting-point and back again to D and finally along the straight line via C back to B . For such a process must the change of entropy vanish. Geometrically this amounts to drawing the graph of the reciprocal of the function \bar{L} against $\frac{U}{A}$, and taking a horizontal straight line in such a position that it cuts off equal areas BEC and CFD .

temperature, v_m the molecular volume and x a dimensionless constant, which for crystals of the NaCl type is equal to $\frac{1}{2} \sqrt{2} \sqrt[3]{4}$, and is, in general, very nearly unity.

It is interesting to notice that this result for ν is closely akin to Lindemann's formula, but has the great theoretical advantage of containing no arbitrary constants. The factor 2.8×10^{12} of Lindemann's expression is in reality a function of the masses and of the nature of the crystal lattice; it should vary from substance to substance. The following table from Braunbek's paper gives his results for a number of typical salts.

Substance	M	$(M_1/M_2)^{\frac{1}{2}} + (M_2/M_1)^{\frac{1}{2}}$	v_m	T_{sm}	ν_o calc.	ν_m calc.	ν_m obs.
KCl	74.6	2.00	37.5	1041	3.4	4.3	4.7
KBr	119.4	2.12	43.4	1001	2.7	3.3	3.6
KI	166.4	2.35	53.3	953	2.3	2.8	3.2
NaCl	58.5	2.05	26.1	1073	4.5	5.9	5.8
AgCl	143.4	2.31	26.0	728	2.7	3.6	3.5
AgBr	187.8	2.02	30.1	697	1.9	2.5	2.6

The ν values are in units of 10^{12} .

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Useful Constants

1μ (unit of wave-length in infra-red)	10^{-4} cms.
Gas constant per gm. mol. R	1.98 calcs. per degree
Avogadro's Number (for one gm. mol.) N	6.06×10^{23}
Boltzmann's constant k	1.372×10^{-16} ergs per degree
Planck's constant h	6.55×10^{-27} ergs-secs.
Frequency constant $\beta = h/k$	4.77×10^{-11} secs.-degree
Stefan-Boltzmann constant σ	1.37×10^{-12} calcs./cms. ² secs. degree
Wien's constant b	0.288 cm. degree
Planck radiation constant c_1	$5.88 \times 10^{-6} \frac{\text{ergs cms.}^2}{\text{secs.}}$
Wien-Planck radiation constant c_2	1.43 cms. degree
Charge on the electron e	4.774×10^{-10} E.S.U.
Mass of the atom of hydrogen m_H	1.65×10^{-24} gms.

Ionic Deformabilities α

	$\alpha \times 10^{24}$
O^{--}	(3.1)
S^{--}	(7.25)
Cl^-	3.05
Br^-	4.17
I^-	6.28
Na^+	0.21
$Ca^{+,+}$	(0.57)

Values in brackets uncertain.

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